PAPERS

STATUS OF THE IMPLEMENTATION OF THE EUROPEAN DIRECTIVE 96/29/EURATOM IN IRELAND IN RELATION WITH NORM

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Abstract

Since the 13th May 2000, following the implementation of the EU Basic Safety Standards Directive 96/29/EURATOM, naturally occurring radioactive materials (NORM) in Irish workplaces are subject to regulations if they are liable to give rise to a radiation dose greater than 1 mSv in a year. The Radiological Protection Institute of Ireland (RPII) is the statutory body in Ireland for matters pertaining to ionising radiation. In 2001, the RPII undertook a review of industrial processes which, on the basis of the literature were thought to lead to enhanced exposure to natural sources of radiation. This paper presents the progress achieved in implementing the legislation for the gas extracting industry and for the peat- and coal-firing power generation.

1. Introduction

In 1996, the European Union Basic Safety Standards Directive [1] included special provisions concerning exposure to natural sources of ionising radiation, recognising the specific problems that need addressing when the source of exposure has not been artificially generated but is of natural origin. In Ireland, the necessary laws and regulations to comply with this Directive were brought into force in May 2000 [2]. Accordingly, work activities where the presence of natural radiation sources (commonly referred to as NORM –Naturally Occurring Radioactive Materials) is liable to give rise to a radiation dose to workers or members of the public greater than 1 mSv in a year are now controlled.

2. Identification of the relevant work activities

2.1. European Commission (EC) guidance

To assist in the identification of the relevant work activities, the EC produced a series of documents mostly limited to consideration of occupational exposures. Radiation Protection 88 [3] recommends to target the work activities listed in Table 1.

Table 1. Examples of work activities, industries and products liable to lead to enhanced exposure to natural sources of radiation [3]

Industry / Work activity	Product / Materials
Coal-mine de-watering plants	Coal and fly ash
Processing of rare earths	MgTh alloys
Fertiliser/phosphoric acid production	Foundry sands (zircon and monazite)
Sulphuric acid production	Refractories, abrasives, ceramics (zirconium minerals)
Smelters (metal production)	Thoriated welding rods and gas mantels
Oil and gas industry	Porcelain teeth
TiO_2 pigment industry	Natural stone
Optical industry and glassware	Fuel peat ash

They mostly involve operations with and storage of materials as well as production of residues not usually regarded as radioactive but which contain naturally occurring radionuclides which could potentially cause a significant increase in the exposure of workers and where appropriate, members of the public. Radiation Protection 95 [4] and Radiation Protection 107 [5] investigate the pathways and the exposure situations which should be looked at when deciding if a work activity potentially falls under the scope of the regulations (Table 2).

Table 2. Most significant NORM industries within the EU, types of materials, pathways and typical exposure situations to be considered ([4]; [5])

Industries	Types of Material	List of Pathways	List of Exposure situations
Phosphate industry; Processing of metal ores; Zircon sands and refractory materials; Extraction of rare earths; Manufacture and use of Th compounds; TiO_2 pigment industry; Oil/gas extraction	Mineral ores By-products, residues Products of the process itself	External irradiation; Inhalation of contaminated dust; Ingestion of dirt and dust; Inhalation of radon diffusing from the material; Skin contamination	Proximity to large amounts of material, little shielding; Dusty conditions, little respiratory protection; Dirty, dusty areas, little protective clothing; Enclosed room, large amounts of materials, little ventilation; **Generic ES1**: stockpiles of material – exposure of warehouse operative **Generic ES2**: residues and scales – exposure of worker removing residues **Generic ES3**: process material in vessels and pipes – exposure of general worker

2.2. NORM industries of relevance in Ireland

In 2001, the Radiological Protection Institute of Ireland (RPII) commenced a programme to identify potential NORM industries currently active in Ireland, based on the above mentioned guidelines (Table 3). Irish industries liable to produce or use diffuse NORM sources include the gas extracting and processing industry, the fossil fuel power production (peat and coal), the bauxite processing/alumina refining industry and a range of other processes producing/using bulk materials with enhanced levels of natural radioactivity (*e.g.* cement, fertilisers, ore extracting industries). Discrete NORM sources identified as being important in an Irish context include thoriated products and natural radioactivity in scrap, which turns up at metal dealers.

Table 3. Irish NORM industries potentially liable to involve NORM

NORM Category	Industry
Diffuse sources	Natural gas extraction and processing Power generation – peat combustion/flyash Power generation –coal combustion/flyash Bauxite processing/alumina refining Cement production Handling of fertilisers
Discrete sources	Use of thoriated products (TIG welding, etc) Metal recycling

At the end of 2001, the RPII started a detailed investigation of the gas extracting/processing industry and of the fossil fuel power production. The results obtained so far are presented in the following sections. For work activities involving NORM, the existence of a radiation risk is usually incidental to the process and the undertaking might not be aware of it. Therefore, it is always necessary to meet the staff management of a particular industry, to discuss the potential occurrence of radiological hazards and to review what a complete or partial radiological assessment will involve.

3. The gas extracting industry in Ireland

The Kinsale Head gas field is located about 50 km off the coastline of County Cork (S Ireland) and was discovered in 1971. It entered into production in 1978. An adjacent gas field (Ballycotton) was discovered in 1989 about 15 km north of Kinsale Head. Between the two of them, they supply approximately 16% of Ireland’s energy requirements. An additional subsea gas well (Greensand) came on stream in 2003 to enhance the productivity of the Kinsale Head gas producing

Greensand reservoir, thereby extending the exhaustion point of the Kinsale Head gas to year 2015. Since December 2003, the Kinsale Head's operator provides firm capacity to process and transport gas extracted from another gas field (Seven Heads) located a further 35 km to the SW of the Kinsale Head field. The Kinsale Head facilities consist of two offshore production platforms, Alpha and Bravo. They both produce and process natural gas for transportation to an onshore metering station. The Bravo platform and the metering station are Normally Unmanned Installations (NUI) [6].

The Corrib gas field is the second large scale exploration project in Ireland. It is situated some 70 km west of the County Mayo coastline (NW Ireland). The operator is currently going through a planning application process in relation to the development of an onshore terminal facility. If the project goes ahead, up to 60% of the Irish domestic gas demand could be met from the Corrib field which has a projected life of 20 years. Unlike the Kinsale Head field, there will be no manned facilities located offshore. All the Corrib's subsea facilities will be controlled and monitored from the onshore terminal via an electro-hydraulic remote control system.

3.1. Recognised issues of radiological significance in the gas industry

Radon (^{222}Rn) is released from the gas reservoir and is transported with the extracted natural gas to the processing plant. In routine operations, as the gas flows continuously through the system and ^{222}Rn decays, its short-lived decay-products (^{218}Po, ^{214}Pb, ^{214}Bi and ^{218}Po) tend to plate out on surfaces that come into contact with the gas to form thin dark grey/black films on the internal side of the equipment ([7]; [8]; [9]; [10]; [11]). The penetrative high energy gamma radiation they emit may result in significant occupational external gamma radiation dose rates in the vicinity of contaminated equipment. During shut downs (repair or maintenance operations), the gas flow stops and within several hours, ^{222}Rn and its short-lived decay-products have decayed. Gamma radiations are no longer emitted but the long-lived decay-products of radon (^{210}Pb, ^{210}Bi and ^{210}Po) remain in the film deposits. These radionuclides emit weak gamma radiation but the energetic alpha emissions of ^{210}Po and ^{210}Pb represent a potential hazard if they become airborne and are ingested or inhaled.

Filter assemblies in gas lines remove radon decay-products from the gas with other particulate matter (heavy-metal decay-products preferentially attach to dust particles and aerosols). Therefore, they could also become radioactive by accumulating residues with enhanced radionuclide concentrations. Sludge accumulating in separator vessels, storage tanks, gas lines and other filter assemblies contain ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Bi and ^{210}Po. Generally, scales do not occur at gas producing facilities as long as formation water is not produced in large quantities. This only happens towards the end of a field’s life [12]. Scale inhibitors are injected in the system when formation water starts to be produced. This can raise the issue, in the future, of possible ^{226}Ra and ^{228}Ra discharges to the environment and contamination of water treatment equipment.

Extracted natural gas is not used directly as it comes from the well. It needs to undergo some processing to remove liquids and/or impurities. Depending on its composition, it might be thermally fractionated to recover Natural Gas Liquids (ethane, propane, butane, and pentane) [10]. As radon has a boiling point between that of ethane and propane, the highest radon levels are generally found in equipment associated with ethane/propane processing [7]. If the natural gas stream does not need to be fractionated (pure methane), ^{222}Rn concentrations in the production stream will remain relatively constant and will only be changed by mixing streams with different concentrations.

For workers involved in the gas producing industry, the greatest risks of exposure occur during shut downs when the production equipment is opened or components are replaced ([10]; [12]). In routine operations, significant exposure to NORM is unlikely to arise as these latter are mostly contained within pipes and vessels and are therefore shielded by the walls of these vessels. However, it is possible that high-energy gamma radiation can pass through the walls of such components and personnel working in close proximity of such equipment could be at risk of receiving a radiation dose.

3.2. Progress of the investigation to date

Radon gas concentrations were measured in all the Irish gas streams at the production point. The results are shown in Table 4.

Table 4. Radon gas concentrations in Irish extracted gas

Gas Field	Radon concentration (Bq·m^{-3})		Measurement location
Kinsale Head (prior to tie-back with Seven Heads gas)	493	average: 696	Alpha platform (inlet separator)
	529		Terminal (export line)
	775 817		Terminal (Calorimeter)
	865		
Seven Heads (prior to tie-back with Kinsale Head gas)	number of measurements: 11; average: 147; range: 39 – 252		Development wells
Combined Kinsale Head/Seven Heads streams	680		Terminal (Calorimeter)
	411		Terminal (Calorimeter) – 3-month measurement (CR-39)
Corrib	Number of measurements: 4; average: 99; range: 25 - 190		Development wells

Samples were collected using a grab sampling technique into previously evacuated Lucas cells. In one case, radon was continuously monitored over a 3-month period (105 days) by means of passive solid state nuclear track detectors (CR-39). Combining all the measurements (excluding Corrib as this field is not producing) gives an average ^{222}Rn concentration in the distributed Irish gas of 590 Bq·m^{-3}. Dixon [13] demonstrated that for typical rates of gas usage and an average radon level of about 200 Bq·m^{-3} at point of use, the estimated dose for domestic users from the use of natural gas was only 4 μSv and for a critical group representing commercial users (commercial kitchens) a few tens of microsievert. Based on these results and on the radon gas concentrations measured in Ireland, it can be concluded that the exposure of the Irish public and employees working in commercial kitchens from the combustion of gas in homes and workplaces is unlikely to give rise to a dose greater than 1 mSv.

It is recognised that a great part of the radioactivity in the gas extracting industry is deposited in sludge in wellhead separators and in water/condensate separation system [14]. Both the Kinsale Head/Seven Heads and the Corrib gases are ‘dry’ and as such are mostly composed of pure methane (98.8% and 93.7% methane for Kinsale/Seven Heads and Corrib, respectively). Therefore, the main processing needed before they can commercially be distributed is dehydration. The Kinsale Head gas does not contain condensate (heavier liquid hydrocarbons extracted from the gas) although there is a possibility that some amount could be produced from the Seven Heads gas. However, at the time of writing, this was not confirmed. It is not possible to predict in advance if condensate will be produced in the Corrib field, but any condensate produced will be re-used as fuel within the Terminal. On the Alpha platform, the separators are inspected every four years on average. It requires shutting down the facilities. After shut down, the production equipment is ventilated and the inside of the vessels is cleaned. Workers are only involved at the end of the cleaning procedure to remove any residues (sludge) deposited at the bottom of the tanks. Sludges are then sent ashore for disposal and the wash down water after the sludge is removed is discharged at sea. In 2003, the amount of sludge sent ashore was approximately 60 kg. The RPII visited the Alpha platform during a shut down to observe the working procedures involved in the cleaning of inlet separators used in the dehydration process. A survey of the equipment (external and internal sides) was originally planned using a range of radiation monitors to determine areas of potential NORM exposure and contamination but this could not be performed for safety reasons and had to be postponed until 2005. Two sludge samples were collected from the bottom of two separators and analysed by high resolution gamma spectrometry (Table 5). Compared with results published in the literature, the Kinsale sludges contain very low levels of natural radionuclides. Van Weers *et al.* [12] for example report that the maximum activity concentrations measured in sludges collected on Dutch platforms were as follow: 800 $Bq \cdot g^{-1}$ ^{226}Ra, 500 $Bq \cdot g^{-1}$ ^{228}Ra, 60 $Bq \cdot g^{-1}$ ^{228}Th. Irish soils on average contain 60 $Bq \cdot kg^{-1}$ of ^{226}Ra [15].

Table 5. Radionuclide composition of sludge samples collected on the Alpha platform. Results are in Bq·kg^{-1} and are quoted on a dry weigh basis

Radionuclide	Sludge 1	Sludge 2
^{234}Th	17.7 ± 3.6	< 6
^{226}Ra	5.5 ± 1.8	< 10
^{214}Pb	7.6 ± 0.8	1.3 ± 0.6
^{214}Bi	7.4 ± 0.8	1.5 ± 0.7
^{228}Ac (^{228}Ra)	15.4 ± 1.2	5.0 ± 1.2
^{228}Th	9.9 ± 8.7	< 17
^{224}Ra	12.6 ± 4.7	< 8
^{212}Bi	13.5 ± 2.7	5.7 ± 4.6
^{212}Pb	11.3 ± 1.3	5.4 ± 0.9
^{208}Tl	3.5 ± 0.4	1.4 ± 0.4

According to the operator, replacement of equipment (pipes, valves, pumps, etc) occurs only when the general layout of the installation needs to be modified, as it was the case when the Seven Heads gas was tied back to the Kinsale Head facilities. Disused equipment is usually stored onshore in a warehouse. A visit of the storage site will be organised in 2005 to carry out a radiation survey and check that surface contaminations (^{210}Pb/^{210}Po), scales/deposits and sludges are not an issue to be considered in the future.

From 2004 onward, discharges of radioactive substances into the OSPAR region from all non-nuclear sectors will have to be reported to the OSPAR Commission [16]. Information requested will include the nature of all discharges (origin, physical and chemical properties including their radionuclide composition) and for the oil and gas industry they will also include the total discharges of radioactive substances from offshore installations (produced water, descaling and decommissioning operations and tracer experiments). For the Kinsale Head gas field, the total volume of produced water discharged at sea in 2003 was 1,830 m^3.

4. The fossil fuel power generation in Ireland

4.1. The peat-fired power production

Annually, approximately 15% of Ireland's electricity requirement is provided through the combustion of 3×10^6 tonnes of peat. While literature on the coal-fired power generation is quite abundant, studies on the peat-fired power generation industry from a radiological point of view are scarce. A study of the largest Irish peat-fired power plant, Shannonbridge (located in the Irish Midlands) was carried out in collaboration with Trinity College Dublin to review the potential occupational radiation exposures arising from the occurrence of NORM at different stages of the industrial process. Ambient gamma dose rate measurements, radon measurements, quantification of the occupational exposure from inhalation of airborne particles and gamma spectrometry analysis of peat, peat ash and effluent samples from the ash ponds were undertaken. Details of the industrial process and results are presented elsewhere [17]. The total annual effective dose likely to be received by a worker involved in the processing of peat and handling of peat ash in Shannonbridge was found to be about 0.3 mSv (312 μSv). Most of the exposure situations where workers are involved on a regular basis were investigated with the exception of maintenance duties like the cleaning of hoppers and freeing of blockages in the grit arrestors. These duties are the only ones where workers are directly in contact with the peat fly ash. However, one would not expect the associated annual effective dose to be significant as this type of work is always carried out with personal protection equipment (PPE), is undertaken in wet conditions to minimise the dust generation, occurs infrequently (3 times in a year) and is usually completed within a week. Another exposure situation is the inhalation of peat ash dust on the landfill sites (generation of windborne ash on the ash pond). This is not included in this study as the top layer of the pond, when dried out, usually forms a crust underneath which the ash is trapped. It is therefore unlikely to be wind blown.

4.2. The coal-fired power production

4.2.1. Description of the industrial process

Moneypoint is the only coal-fired power generating station in Ireland. It is located in the West of the country, along the Shannon estuary. It consumes 2×10^6 tonnes of world trade coal per annum and produces 40% (total capacity of 915 MW) of the total Irish demand in electricity. On its arrival at the plant, the coal is stored outdoor in a stockyard protected with a wind barrier. Two conveyor belt systems carry the coal from the stockyard to the boiler bunkers. From there, the principles of combustion and production of ash are similar to those described for the peat-firing power generation [17]. Coarse ash (bottom ash) is collected under the furnace and pulverised fly ash (PFA) is collected by electrostatic precipitators (ESPs). About $180\text{-}200 \times 10^3$ tonnes of ash are produced annually at Moneypoint, of which 85% is PFA and the remaining 15% bottom ash. Approximately 100×10^3 tonnes of PFA are sold annually to the cement industry. It enters in the composition of the cement for 5 to 10%, as a shale substitute. The remaining PFA is conditioned on site with water (to prevent dust generation) and transferred by truck to the disposal area (total capacity of 3×10^6 m^3, approximately 10 m deep) in dry condition. The bottom ash is hydraulically transferred from the plant in a slurry form, dewatered in silos, loaded into trucks and transferred to the landfill area where it is kept separate from the PFA. Truck drivers and workers on the landfill wear dust masks. The disposal area is regularly checked for groundwater testing by the Irish Environmental Protection Agency.

4.2.2. Radiological protection issues

Clearly, the radiation doses received by individual workers at coal-fired power stations vary substantially depending on their duties, with the majority receiving trivial doses. This is illustrated by the results of the study carried out by the NRPB [18], which considered parameters such as routine operation, atmospheric releases, discharges to landfill and sales of ash. This study found that the radiological impact on the UK population of the coal-fired industry was low, with two exceptions: the use of coal ash in building materials and the possibility of high levels of naturally occurring radionuclides in scales on boiler tubes. These conclusions provided the basis of an investigation initiated by the RPII in 2003 to determine if the work activities carried out at Moneypoint were giving rise to doses liable to exceed 1 mSv to any individual in a 12 month-period.

Over the last 15-20 years, a number of studies and measurements of coal and coal ash samples have been carried out through collaborations between Moneypoint (Electricity Supply Board), the RPII, Trinity College Dublin and University College Dublin (Table 6).

Table 6. Radionuclide composition (in Bq·kg^{-1}) of coal processed in Moneypoint and comparison with coal processed in other countries

	Country of origin of coal	**^{238}U**	**^{226}Ra**	**^{210}Pb**	**^{232}Th**	**^{40}K**
Moneypoint	Poland	45	39-86	20-32	11-12	80
	Australia		25-40		2-13	20-50
	USA	5-32	6-60	10-16	5-12	30-75
	Columbia		25-30		3-9	80-100
	UK	14	24	27	8	75
[18]	UK average	20	15-20	20	7.5	
[19]	Poland	38			30	290
	Australia	30-48			30	40
	USA	18			21	52
	UK	15			13	150
[20]	Hungary	300-500				
[21]	Brazil	24-35			27-48	351-447

The ^{238}U-series is generally in equilibrium in the coal, apart from a reduction in concentration of the later daughter nuclides due to a loss of radon during the combustion process. For each radionuclide, significant variations of activity concentrations can be observed. This is more than likely due to the different country of origin of the coal supplies. Despite this variability, activity concentrations averaged over one year of power production are generally constant.

Radionuclide concentrations in PFA are consistently higher, by a factor of ten or so, compared to those in coal (Table 7). This is because at furnace temperatures, some elements originally contained in the coal are partly or completely evaporated. Between the furnace and the ESPs, the gas and fly ash stream is cooled down to remove the heat from the gas prior to its emission to the atmosphere. As the flue gases cool down, the volatilised elements condense onto the fly ash particles, giving rise to an enrichment of their concentrations in the fly ash trapped by the ESPs.

Table 7. Radionuclide composition (in Bq·kg^{-1}) of coal ash produced in Moneypoint and comparison with ash produced in other countries

Coal origin and/or [References]		**^{238}U**	**^{226}Ra**	**^{210}Pb**	**^{232}Th**	**^{40}K**
Moneypoint	1986-1990 (average) [22]	120	134	89	53	650
	1993 (average) [23]	116	118		69	545
	USA (2002) [24]	73	137	83	72	536
	Columbia (2002) [24]	46	71	37	34	235
	Australia (2002) [24]	52	113	69	64	155
	Indonesia (2002) [24]	72	118	105	90	229
[18]	UK Measurements range	43-110	44-74	98-188	19-40	
	Used for dose calculations	100	100	100-200	50	900
[25]	EU arithmetic mean		230		100	570
[20]	Hungary	1000-1500	Approx. 1400			
[26]	Poland	116-156	86-104	112-183	66-84	608-720
[27]	Greece	Up to 1443	273-1377	Up to 3986	41-65	143-661
[28]	Australia		96		170	203

The activity concentrations of the coal processed and the ash produced in Moneypoint do not differ significantly from the ones used in [18]. Therefore, assuming similar industrial processes in Ireland and the UK, the conclusions reached in [18] should also apply to the Irish coal-fired electricity generation.

Only a small fraction of the fuel gases that contain radionuclides in gaseous form passes through the ESPs and is then discharged through the stack to the atmosphere. On average 12% of the total ash (and non-volatile elements) is removed in the furnace (bottom ash) and about 87% is removed in the ESPs (PFA). This gives a total removal in excess of 99%. Specific emissions of particulate matter are on average below 80 $mg \cdot m^{-3}$, which corresponds to an emission rate of about 20 g of ash per second from each unit at 305 MW output ([29], Table 8).

Table 8. Fly ash annual emission into the air (downstream of the ESPs) for 5 different types of coal, assuming 7,500 full load hours [29]

Indonesia	South Africa	Australia	Columbia	East USA
386 $t \cdot y^{-1}$ per boiler	585 $t \cdot y^{-1}$ per boiler	229 $t \cdot y^{-1}$ per boiler	71 $t \cdot y^{-1}$ per boiler	225 $t \cdot y^{-1}$ per boiler

It is this fraction of the fly ash as well as the gaseous fraction that preferentially deposits in the pulmonary and bronchial regions of the respiratory tract and this could be an issue of concern for members of the public because of the preferential enrichment in ^{210}Po and ^{210}Pb onto the finer fly ash particles. The off-site radiological effects of the Moneypoint's operation were investigated between 1986 and 1990 using a gaseous dispersion model of radiologically active trace elements in the Moneypoint plume [30]. They were found negligible.

According to Smith *et al.* [18], comparing the doses arising from building materials containing 30% ash (with activity concentrations quoted in Table 7) with the doses arising from materials not containing ash leads to a predicted excess external dose to that received outdoors of 600 $\mu Sv \cdot y^{-1}$ after subtraction of external background. This is within the range of 0.3 to 1 $mSv \cdot y^{-1}$ for which the EC guidance indicates that controls on the use of such building materials should be instituted ([25]; [31]). Trinity College Dublin is currently investigating the significance and the extent of external doses arising from building materials containing coal ash commonly used in Ireland.

In 2001, Huijbregts *et al.* [32] reported the occurrence of scale deposits on the outside of pipes within boilers of coal-fired power stations, which contained ^{210}Pb at levels exceeding the Dutch regulatory limit of 100 Bq·g^{-1}. Both the rate of accumulation and the composition of the scale were found to be very dependent upon the chemical environment and the temperature inside the boilers. Smith *et al.* [18] conservatively estimated that a scale with a ^{210}Pb concentration of 100 Bq·g^{-1} could give rise to doses in the region of 100 μSv·y^{-1} for workers involved in boiler maintenance. On average, the coal processed in Moneypoint has a lower chlorine content (< 2%) than the coal processed in the Dutch study. High chlorine contents favour the establishment of reducing conditions in the boilers which in turn lower the temperature of condensation for Pb (660°C instead of 880°C in oxidising conditions). The Moneypoint boilers also operate at higher stoechiometry than the ones used in the Netherlands because they are fitted with first generation of low NO_x burners which operate in oxidising conditions. Finally, the boilers currently in use in Moneypoint are smaller in size than in the Netherlands, which means that higher combustion temperatures are prevailing in Moneypoint. This increases the chance to exceed the condensation temperature of 880°C for Pb, thereby decreasing the chance of Pb condensation on the waterwall tubes inside the boilers. For all these reasons, the build-up of scales and therefore the potential existence of increased levels in ^{210}Pb in the Moneypoint boilers were ruled out [33]. In order to reach the future European standard for low NO_x emissions, the current generation of boilers will have to be replaced by the 1st January 2008 by a second generation of large-size boilers operating in forced reducing conditions. This means that from 2008 onward, the occurrence of scales will have to be controlled and monitored on a regular basis.

Radon concentrations in air at different locations throughout Moneypoint were measured in 1988. All the readings were found to be well below the Irish regulatory limit of 400 Bq·m^{-3}. The RPII requested to have a more complete radon survey being carried out to assess the radon concentrations on the totality of the premises, including offices, workshops, etc. Sixty passive solid state nuclear track detectors (CR-39) were dispatched on site for a period of 3 months and returned for analysis. They are currently being processed.

5. Future investigations

The largest bauxite processing plant in Western Europe is located in the West of Ireland. It produces annually approximately 1 × 10^6 tonnes of alumina from 2 × 10^6 tonnes of bauxite. A radiological assessment of the industrial process, feeding material, waste streams and work practices will be carried out. In 1992, O'Grady [34] surveyed fertiliser handling practices in Ireland and estimated the radiation doses to workers involved in manufacture, transport and storage, to farm-workers and to members of the public. This study concluded that, since the cessation of phosphoric acid production in Ireland in 1981, the dose to the most exposed individual was unlikely to exceed 100 μSv per year and, on average, was well below this. Thorium is used as an additive in a number of industrial processes to improve heat stability of metal alloys. In the welding industry thorium is added to electrodes used in tungsten inert gas (TIG) welding to facilitate arc starting and to increase arc stability. TIG welding has particular advantages in stainless fabrication work and is widely used in Ireland for this purpose. Ludgwig *et al.* [35] showed that in some cases the exposure to operators involved in welding and grinding could exceed 1 $mSv \cdot y^{-1}$. Following an incident involving the scrapping of a radiocaesium source in the early 90s, portal monitoring was installed at the only steel plant operating in Ireland at that time [36]. Up until the closure of the plant in May 2001, the RPII was notified of alarm activations approximately once a month and radioactive sources in scrap metal were regularly identified, the majority of which were found to be NORM materials. Dismantling/decommissioning activities of major industries such as the Irish Fertiliser Industry (IFI) and the replacement of disused equipment in still active industries (cement industry) need to be monitored and controlled for the presence of NORM contamination. Finally, disused mines and industries/companies involved in the use and transport of zircon sands and titanium dioxide will also have to be identified and reviewed.

6. Conclusions

Since May 2000 and the incorporation into Irish law by Ministerial Order of the European Basic Safety Standards Directive, industries liable to involve work activities resulting in significant exposure to natural radiation sources are subject to regulation if they are liable to give rise to a radiation dose greater than 1 mSv in a year. The gas extracting industry, the peat and coal-fired power generation were the first industries to be investigated by the RPII. To date and based on the results of field and laboratory measurements, none was found to be of radiological concern, although work is still on-going for some of the issues raised. Investigation of the bauxite processing/alumina refining industry is due to commence before the end of the current year while the TIG welding industry, disused mining activities and dismantling/decommissioning operations will be dealt with a later stage.

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References

1. Council of the European Union, Basic Safety Standards for the Health Protection of the General Public and Workers Against the Dangers of Ionising Radiation, Council Directive 96/29/EURATOM, Luxembourg (1996).
2. Stationery Office, Radiological Protection Act, 1991 (Ionising Radiation) Order. Statutory Instrument 125 of 2000, Department of Public Enterprise, Government Publications Office, Dublin (2000).

3. European Commission, Recommendations for the implementation of Title VII of the BSS concerning significant increase in exposure due to natural radiation sources. Radiation Protection 88. EC Directorate-General Environment, Luxembourg (1997).

4. European Commission, Reference levels for workplaces processing materials with enhanced levels of naturally occurring radionuclides: a guide to assist implementation of Title VII of the European BSS Directive concerning Natural Radiation Sources. Radiation Protection 95. EC Directorate-General Environment, Luxembourg (1999).

5. Penfold, J.S.S., Mobbs, S.F., Degrange, J.P., Schneider, T., Establishment of reference levels for regulatory control of workplaces where materials are processed which contain enhanced levels of naturally-occurring radionuclides. Radiation Protection 107. EC Directorate-General Environment, Luxembourg (1999).

6. Carroll, K., Gas storage - More energy in store. Institution of Engineers of Ireland (IEI), The Engineers Journal, Issue Nov. 2002 (2002).

7. Summerlin, J.Jr., Prichard, H., Radiological health implications of Lead-210 and Polonium-210 accumulations in LPG refineries. Am. Ind. Hyg. Assoc. J., 46 (4): 202-205 (1985).

8. Gray, P.R., NORM contamination in the petroleum industry. J. of Petroleum Industry, 45(1): 12-16 (1993).

9. American Petroleum Institute, Bulletin on Management of NORM in oil and gas production, API Bulletin E2, First Ed. (1992).

10. Gesell, T.F., Occupational radiation exposure due to ^{222}Rn in natural gas and natural gas products. Health Physics, 29:681-687 (1975).

11. Bjørnstad, T., Ramsøy, T., The “invisible” radioactive scale, Proceedings of the 10th International Oil Field Chemicals Symposium, Norwegian Society of Chartered Engineers, Oslo, 195-211 (1999). [available online at www.ife.no]

12. van Weers, A.W., Pace, I., Strand, T., Lysebo, I., Watkins, S., Sterker, T., Meijne, E.I.M., Butter, K.R., Current practice of dealing with natural radioactivity from oil and gas production in EU Member States, Report EUR 17621 EN, Nuclear Safety and the Environment, European Commission, Luxembourg (1997).

13. Dixon, D.W., Radon exposures from the use of natural gas in buildings. Rad. Prot. Dos., 97(3): 259-264 (2001).

14. Scholten, L.C. Approaches for regulating management of large volume of waste containing natural radionuclides in enhanced concentrations, Report EUR 16956 EN, Nuclear Safety and the Environment, European Commission, Luxembourg (1996).

15. Marsh, D., Radiation mapping and soil radioactivity in the Republic of Ireland, MSc. Thesis, Trinity College, National University of Ireland, Dublin (1991).

16. RSC 2004, Summary Records [available online at www.ospar.org, Zip File].

17. Organo, C., Lee, E.M., Menezes, G., Finch, E.C., Investigation of the peat-fired power generation in Ireland, NORM IV Conference, 16-21 May 2004, Szczyrk, Poland.

18. Smith, K.R., Crockett, G.M., Oatway, W.B., Harvey, M.P., Penfold, J.S.S., Mobbs, S.F., Radiological impact on the UK populations of industries which use or produce materials containing enhanced levels of naturally occurring radionuclides: Part I: Coal-fired Electricity Generation, Report NRPB-R327, National Radiological Protection Board, Chilton, Didcot (2001).

19. United Nations Scientific Committee on the Effects of Atomic Radiation, Sources and Effects of Ionizing Radiation. Report to the General Assembly, with Scientific Annexes. United Nations, New York (2000).

20. Papp, Z., Dezso, Z., Daroczy, S., Significant radioactive contamination of soil around a coal-fired thermal power plant. J. Environmental Radioact., 59: 191-205 (2002).

21. Flues, M., Moraes, V., Mazzilli, B.P., The influence of a coal-fired power plant operation on radionuclide concentrations in soil. J. of Environmental Radioactivity, 63: 285-294 (2002).

22. McAulay, I.R., Department of Physics, Trinity College Dublin. Unpublished data (1986-1990).

23. Electricity Supply Board (ESB), Moneypoint, Personal Communication (2003).

24. Lee, E.M., Department of Physics, Trinity College Dublin, Personal Communication (2002).

25. European Commission, Enhanced radioactivity of building materials. Radiation Protection 96. Directorate-General Environment, Luxembourg (1999).

26. Bem, H., Wieczorkowski, P., Budzanowski, M. Evaluation of technologically enhanced natural radiation near the coal-fired power plants in the Lodz region of Poland. J. of Environmental Radioactivity, 61: 191-201 (2002).

27. Petropoulos, N.P., Anagnostakis, M.J., Simopoulos, E.E., Photon attenuation, natural radioactivity content and radon exhalation rate of building materials. J. of Environmental Radioactivity, 61: 257-269 (2002).

28. Beretka, J., Mathew, P.J., Natural radioactivity of Australian building materials, industrial washes and by-products. Health Physics, 48(1): 87-95 (1985).

29. Meij, R., Emission testing including mass balances of representative coals at Moneypoint power stations, KEMA Report (TSA Power Generation and Sustainables), Arnhem (2003).

30. Electricity Supply Board (ESB), Nuclear Energy Board (NEB), Unpublished data (1986-1990).

31. European Commission, Practical use of the concepts of clearance and exemption – Part II Application of the concepts of exemption and clearance to natural radiation sources. Radiation Protection 122. Directorate-General Environment, Luxembourg (2001).

32. Huijbregts, W.M.M., de Jong, M.P., Timmermans, C.W.M., Hazardous accumulation of radioactive lead on the water wall tubes of coal-fired boilers. Anti-corrosion Methods and Materials, 7(5): 274-279 (2000).

33. McCarthy, F., Electricity Supply Board (ESB), Moneypoint, Personal Communication (2003).

34. O'Grady, J., Radioactivity and fertilisers. Technology Ireland, 24:41-45 (1992).

35. Ludgwig, T., Schwaß, D., Seitz, G., Seikmann, H., Intakes of thorium while using thoriated tungsten electrodes for TIG welding. Health Physics, 77(4): 462-469 (1999).

36. O'Grady, J., Hone, C., Turvey, F.J., Radiocaesium contamination at a steel plant in Ireland. Health Physics, 70(4): 568 (1996).

INVESTIGATION OF THE PEAT-FIRED POWER GENERATION IN IRELAND

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Abstract

Annually, approximately 15% of Ireland's electricity requirement is provided through the combustion of 3×10^6 tonnes of peat. While literature on the coal-fired power generation is quite abundant, studies on the peat-fired power generation industry from the radiological point of view are scarce. A study of the largest Irish peat-fired power plant was initiated to review the potential occupational radiation exposures arising from the occurrence of Naturally Occurring Radioactive Materials (NORM) at different stages of the industrial process. Ambient gamma dose rate measurements, radon measurements, quantification of the occupational exposure from inhalation of airborne particles and gamma spectrometry analysis of peat, peat ash and effluent samples from the ash ponds were undertaken. The results indicate that the plant workers are unlikely to receive a radiation dose above 300 µSv per annum over the typical working hours.

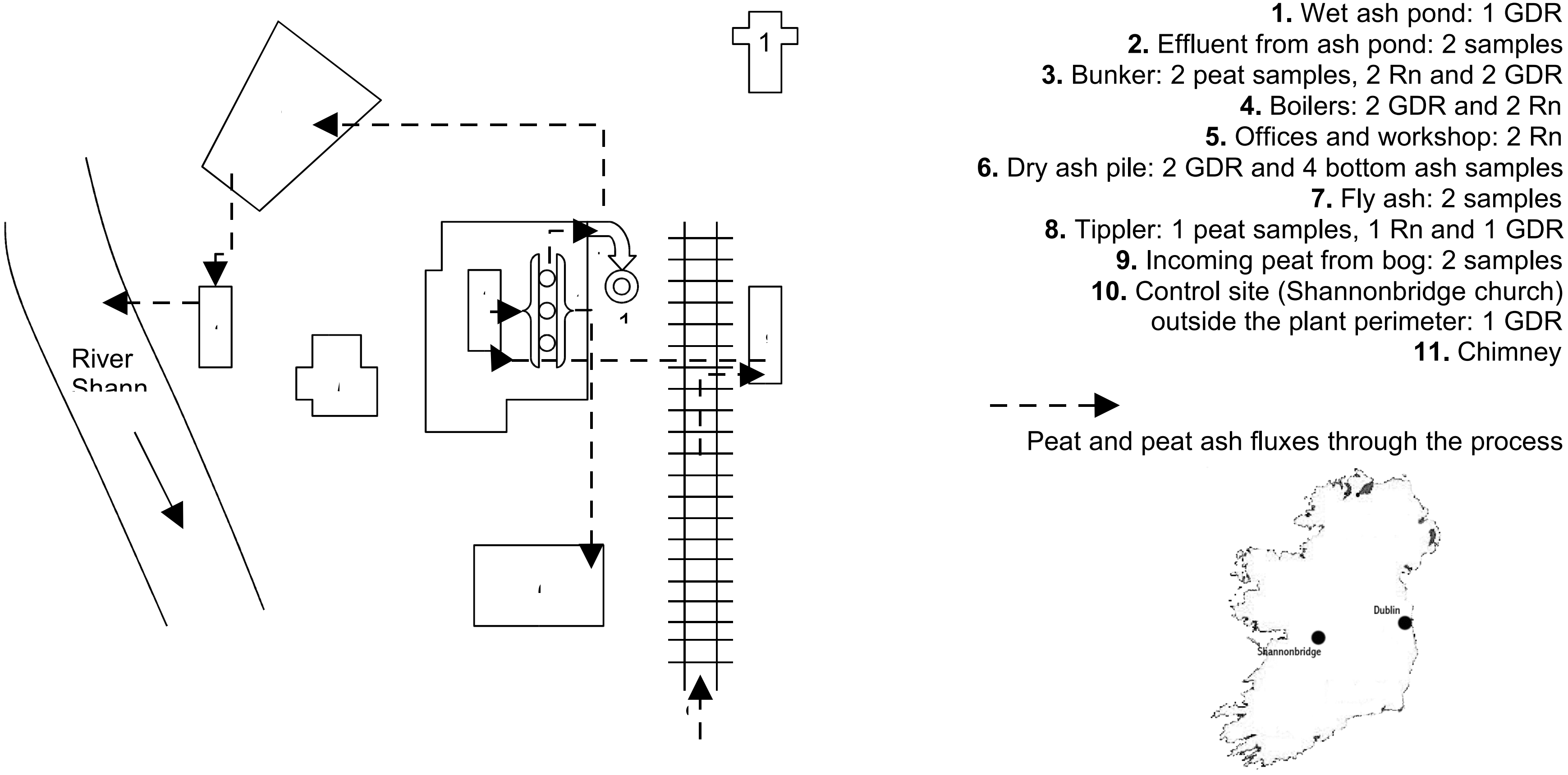
1. Introduction

Around 90% of human radiation exposure arises from natural sources such as cosmic radiation, exposure to radon gas and terrestrial radiation. However, some industries processing natural resources may concentrate radionuclides to a degree that they may pose risk to both humans and the environment if they are not controlled. In May 2000, legal controls were introduced in Ireland covering work activities where the presence of natural radioactivity could lead to the risk of a significant increase in exposure to workers or members of the public. These controls are set out in the Radiological Protection Act, 1991 (Ionising Radiation) Order. Statutory Instrument 125 of 2000 [1] and hereafter referred to as S.I. 125 of 2000, which implements the European Union Basic Safety Standards Directive 96/29/EURATOM [2]. Article 3 of S.I. 125 of 2000 in particular provides for the regulation of naturally occurring radioactive materials in the workplace, mostly of terrestrial origin and hereafter referred to as NORM, if they are liable to give rise to a radiation dose greater than 1 mSv in a year. In 2001, the Radiological Protection Institute of Ireland (RPII) initiated a programme to identify industries currently active in Ireland which, on the basis of the literature, were considered liable to involve work activities resulting in exposure to diffuse NORM sources. To date, they include the gas extracting industry, the fossil fuel (peat and coal) power production and a range of industrial processes using bulk materials with enhanced levels of natural radioactivity (*e.g.* bauxite refining). A joint study was designed in collaboration with the Physics Department of Trinity College Dublin to determine the radioactivity levels in Irish peat and peat ash, compare the results with similar studies in other countries and with national and international legislation and investigate the extent of any radiation exposure of workers arising from the handling, burning and storage of peat ash. Environmental exposure to elevated levels of radionuclides resulting from the gaseous emissions from the stack was not investigated.

2. The Irish peat-fired power generation

Until recently, up to nine peat-fired power plants were in operation in Ireland. By the end of 2004, this generation of power stations built between 1950 and the early 80s will be replaced by two newly-built power plants processing just over 2 × 10^6 tonnes of peat per annum between the two of them. This study was undertaken at the largest existing peat-fired power station in the country, Shannonbridge. It is located in the Midlands region (Figure 1) and has been operating since 1965. The current plant consumes approximately 1.1-1.2 × 10^6 tonnes of peat per annum and produces 125 MW of electricity. On average, 20 to 25 × 10^3 tonnes of peat ash are produced every year (1/3 of the total ash produced by all the Irish peat-fired plants). Five million tonnes of ash are currently landfilled on site at the plant. The Irish Peat Board (Bord na Móna) supplies the milled peat to Shannonbridge from a local bog where it is mechanically harvested by scraping the top of the bog to a depth of up to 30 cm, milled (72 mesh), solar dried and transported to the power station by light rail. Each convoy of 15 wagons carries 75 tonnes of peat. On arrival at the plant a “tippler” unloads each wagon sequentially into a hopper from where the peat is transferred by conveyor belts into the plant. At this stage, the peat is milled further into a fine dust and blown into the furnaces for combustion in suspension at about 1,000-1,100°C. Approximately 5-10% of the total ash produced falls below the furnace as 'bottom ash'. The remaining 90-95% passes into the flue gas stream as 'fly ash'.

Figure 1. Schematic sketch of the Shannonbridge peat-fired power plant with locations of the measurements undertaken and samples analyzed during this study (the scale of the objects are not respected) – GDR = gamma dose rate measurement, Rn = radon measurement. A map of Ireland is inserted to show the location of Shannonbridge



1. Wet ash pond: 1 GDR
2. Effluent from ash pond: 2 samples
3. Bunker: 2 peat samples, 2 Rn and 2 GDR
4. Boilers: 2 GDR and 2 Rn
5. Offices and workshop: 2 Rn
6. Dry ash pile: 2 GDR and 4 bottom ash samples
7. Fly ash: 2 samples
8. Tippler: 1 peat samples, 1 Rn and 1 GDR
9. Incoming peat from bog: 2 samples
10. Control site (Shannonbridge church) outside the plant perimeter: 1 GDR
11. Chimney

- - - ▶ Peat and peat ash fluxes through the process

This gaseous-particulate mixture leaves the furnace and is drawn through a series of grit arrestors designed to retain about 90% of the fly ash and any unburned carbon. At furnace temperatures, some elements originally contained in the peat are partly or completely evaporated. Between the furnace and the grit arrestors, the gas and fly ash stream passes over banks of tubes containing water or air to give a more efficient removal of the heat from the gas prior to its emission to atmosphere. As the flue gases cool down from 1,000 to 200°C, the volatilized elements condense onto the fly ash particles, giving rise to an enrichment of their concentrations in the fly ash trapped by the grit arrestors. Only a small fraction of the fuel gases containing small quantities of radionuclides in gaseous form passes through the grit arrestors and is discharged through the stack to the atmosphere. Sampling of fly ash is possible only when the boilers are not in operation. The number of samples that could be obtained was therefore limited. In Shannonbridge, the bottom ash is disposed of in 'wet' or 'dry' conditions. ‘Dry’ bottom ash is produced by two of the three furnaces in operation. It is transported in a trailer attached to a tractor to a dry ash pile. ‘Wet’ bottom ash from the third furnace is hydraulically piped out by flexible tubing to two nearby wet ash ponds together with the totality of the fly ash trapped in the grit arrestors. In the ponds, the ash resides in a 50% minimum aqueous environment to minimize the production of airborne particles.

3. Materials and methods

Gamma spectrometry analysis of peat, peat ash and effluent samples collected at the plant, airborne peat dust analysis, aerial radon gas measurements and ambient gamma dose rate measurements were carried out. Samples for gamma spectrometry analysis were counted in Marinelli geometry and analyzed using a low background n-type HPGe GMX gamma-ray detector (relative efficiency of 34%, resolution of 2 keV (FWHM) at 1.33 MeV). Each sample was counted for a 24-hour period. Activity concentrations of ^{238}U-series radionuclides, ^{232}Th, ^{40}K and

^{137}Cs were determined. Ra-226 activities were ascertained using the two gamma-ray lines at 93 keV and 186 keV, corrected for the interference of ^{235}U at 186 keV. Th-232 was determined from the gamma-ray emissions at 911, 969, 338, 965, 795, and 463 keV from ^{228}Ac. K-40 and ^{137}Cs activities were determined from their respective lines at 1461 keV and 662 keV. Airborne peat dust concentration was measured in the plant to assess the potential radiation dose through inhalation of airborne particles. A filtration sampling method (AEA Technology filter holder, Casella London Ltd.) was used, where a known volume of air is drawn through a pre-weighed glass fibre filter paper (25 mm diameter, pore size 80 µm) by means of an air pump. On site, the filter holder was placed in a static position at approximately 1.60 m high (breathing zone height). The flow rate of the pump was set at 2 litres per minute and the pump was allowed to run from 9.30 am until 5.15 pm (standard work shift). Passive long-term radon measurements were carried out to determine if the concentrations exceeded the national Reference Level for workplaces, 400 $\text{Bq}\cdot\text{m}^{-3}$ averaged over a minimum period of 3-months. Passive alpha track detectors consisting of a two-part polypropylene holder and a CR-39 (poly allyl diglycol carbonate) detection plastic were used. Upon completion of the measurements the tracks recorded on the plastics are analysed and counted using a Leitz Ergolux AMC microscope coupled to a Leica Quantimet Q520 image analysis system. A track density is determined for each plastic and converted into radon concentration C ($\text{Bq}\cdot\text{m}^{-3}$) after subtraction of a fixed background value and taking into account a pre-determined calibration factor as well as the exposure duration. A seasonal correction is applied to C when the detectors are exposed for less than twelve months [3]. Gamma dose rate measurements were carried out using a NE Technology portable gamma dose rate meter (type PDR1) and a Mini Instruments integrating Geiger Müller-Background Monitor-Type 6-80 (GM6-80). Instantaneous gamma dose rate readings were taken with the PDR1 meter and an average value was calculated from the lowest and highest readings. The GM6-80 meter was fixed to a tripod at each location for 1000 seconds. The readings were converted to an ambient gamma dose rate ($\mu\text{Sv}\cdot\text{hr}^{-1}$) using a calibration conversion table relevant to the instrument.

4. Results

4.1. Peat, peat ash and effluent from the wet ash pond

If the activity concentrations of radionuclides present in the ash are significant there could be a potential for increased radiation exposure to workers handling and working with the ash. Radionuclide analysis of peat, bottom ash and fly ash from Shannonbridge indicate a great variability of activity concentrations (Table 1). In general, fly ash presents significantly higher concentrations than the bottom ash in the U-series, while the bottom ash contains more ^{40}K than the fly ash. Table 2 shows that there is a wide range of activities between the fly ash produced at different peat-fired power stations in Ireland [8]. Compared with other types of NORM or with the average Irish soils, it is clear that the peat and the peat ash produced in Shannonbridge contain lower levels of naturally occurring radionuclides.

Table 1. Specific activities of U-series radionuclides, ^{232}Th, ^{40}K and ^{137}Cs (in Bq·kg^{-1}, dry weight) measured in the peat, peat ash and effluent from the ash pond. Errors quoted are the counting uncertainties at one standard deviation from the mean count. BDL = Below Detection Limit of 0.19 Bq·kg^{1}

Sample Type	^{238}U	^{234}Th	^{226}Ra	^{214}Pb	^{210}Pb	^{232}Th	^{40}K	^{137}Cs
PEAT								
entering plant	2.8±0.4	4.3±0.6	2.6±0.4	4.4±1.0	18.8±1.5	BDL	6.1±5.7	4.2±0.1
entering plant	4.0±0.3	2.0±0.2	1.8±0.1	0.5±0.1	5.0±0.6	0.4±0.0	BDL	2.2±0.1
in tippler	10.9±5.3	14.1±1.0	6.3±3.1	3.8±0.6	27.3±1.6	BDL	6.5±2.9	12.3±0.3
in bunker	7.4±3.9	10.8±1.0	5.4±2.8	2.2±0.4	37.8±2.6	BDL	BDL	11.5±0.3
dust in bunker	BDL	3.8±0.4	4.3±0.2	1.6±0.1	23.8±1.6	BDL	BDL	BDL
MAX VAL	*15*	*15*	*10*	*5*	*50*	*1*	*10*	*20*
FLY ASH								
	301.2±13.9	306.3±5.8	28.9±1.4	59.2±0.9	225.9±10.4	7.27±0.4	66.5±2.0	67.5±1.0
	52.1±1.4	115.1±7.6	32.2±0.9	41.7±6.3	297.0±14.9	BDL	BDL	BDL
MAX VAL	*300*	*300*	*50*	*70*	*350*	*10*	*50*	*50*

BOTTOM ASH								
	77.1±13.8	33.0±0.9	14.9±1.4	3.8±0.1	13.9±0.8	BDL	7.6±0.8	4.8±0.1
	67.9±2.9	19.6±1.1	7.2±0.3	13.5±0.4	211.1±9.1	4.2±1.3	185.0±19	104.0±1.6
	32.1±3.2	29.3±2.9	19.3±2.0	9.8±0.2	167. 3±6.0	2.8±0.8	121.0±30	92.3±1.4
	9.1±0.6	7.1±0.8	6.3±0.4	0.3±0.1	8.2±1.0	0.59±0.1	BDL	BDL
MAX VAL	*100*	*50*	*20*	*20*	*250*	*5*	*200*	*150*
EFFLUENT								
	0.31±0.1	2.9±0.5	BDL	0.5±0.1	3.0±0.3	BDL	BDL	0.6±0.0
	BDL	1.1±0.1	0.7±0.1	BDL	0.27±0.2	BDL	BDL	BDL

Table 2. Comparison of the results from this study and other references in the literature (activity concentrations in Bq·kg^{-1})

Sample Type	^{238}U	^{234}Th	^{226}Ra	^{210}Pb	^{232}Th	^{40}K	^{137}Cs	References
RAW MATERIAL								
Irish peat	***15***	***15***	***10***	***50***	***1***	***10***	***20***	This study
Finnish peat	16		11	30	5.3	28	27	[4]
Coal Moneypoint	19 (5-45)		30 (6-67)	14 (4-27)	8 (2-13)	61 (20-100)		[5]
Coal UK	15	15	15	15	7.5	144		[6]
Coal world average	24				22	100		[7]
FLY ASH								
This study	***300***	***300***	***50***	***350***	***10***	***50***	***50***	This study
Peat Shannonbridge	133		71		7	32	130	[8]
Peat Ferbane	290		121		11	112	20	[8]
Peat Lanesborough	74		68		14	263	79	[8]
Peat Rhode	121		127		8	57	127	[8]
Peat Bellacorick	38		31		10	153	47	[8]
Peat Finland			120		46	390		[9]
Coal Moneypoint	110		156	79	68	445		[5]
Coal UK	100	100	100	100-200	50	900		[5]
BOTTOM ASH								
This study	***100***	***50***	***20***	***250***	***5***	***200***	***150***	This study
Coal Moneypoint	73		84	23	43	307		[5]
Coal world average			85		61	510		[6]
OTHER NORM								

Bauxite Boké		78	110		[10]
Bauxite	400-600		400-600		[11]
Red mud	260-540		340-500		[12]
Red mud		250	300		[13]
Phosphogypsum		1000			[14]
Phosphate ore		30-5000	20-2000	3-200	[11]
Zircon sands		3000-4000	10000		[11]
Average Irish soils		46	25	418	[15]

With regard to the radioactivity enhancement in the fly ash and the bottom ash arising from the combustion process, some radionuclide concentrations could be enhanced by a factor 20 to 25 compared with concentrations in the original peat as indicated in [16]. Pb-210 shows the largest enrichment onto small fly ash particles (< 1.3 µm) according to Mustonen and Jantunen [4], indicating a volatile behaviour at the furnace temperature. Enrichment factors (*EF*) for different radionuclides can be calculated using the formula:

$$EF = \frac{[c_r]_{ash}}{[{}^{226}Ra]_{ash}} \Bigg/ \frac{[c_r]_{peat}}{[{}^{226}Ra]_{peat}} \qquad (1)$$

where $[c_r]$ and $[{}^{226}Ra]$ are the activity concentrations of a potentially enriched (or depleted) radionuclide *r* and ^{226}Ra, respectively. Ra-226 is used as a reference nuclide because of its non-volatile nature at furnace temperature [4]. To simplify the calculations, a single activity concentration for each radionuclide in the peat, in the fly ash and in the bottom ash was assumed by rounding up to the maximum concentration measured (conservative end of the range of concentrations measured). The values are displayed in italics in Table 1 where they are quoted as *MAX VAL*. *EF* values in the fly ash were calculated to be 1.4, 4, 2, 1 and 0.5 for

^{210}Pb, ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs, respectively. For the same radionuclides, *EF* values in the bottom ash are 2.5, 3.3, 2.5, 10 and 3.75.

4.2. Airborne dust concentration

The dustiest location of the plant was found to be the bunker, an indoor-type of warehouse where a 4-hour supply of milled peat is temporarily stored at any time before it is fed into the mills. In this area, employees are carrying out dry sweeping duties of spilled peat dust, regularly generating large amounts of fine airborne dust. A single air sampling experiment over an 8-hour working shift was carried out during which the dust concentration was measured at 25.6 mg·m^{-3}. This is very significant in terms of occupational dust exposure (the Irish Occupational Exposure Limit (OEL) for nuisance dust is set at 10 mg·m^{-3} [17]). Employees working in this area are required to wear personal protection equipment (PPE) including protective clothing and a face dust mask. They also only work in this location for very short periods of time.

4.3. Radon gas

In industries dealing with diffuse NORM an important radiation exposure pathway can be radon and radon daughters' inhalation from storage of large volume of materials. This is because these materials are often crushed or powdered before they are processed (allowing for radon to escape more easily from the matrix) and may be stored in poorly ventilated spaces (allowing radon concentrations to build up). The associated radiation dose may substantially vary as it is strongly dependent on a wide range of parameters such as the emanating fraction, the dose equilibrium factor, the dose conversion factor, the ventilation rate, the room size, the surface to volume ratio and the diffusion coefficients [13]. Two radon surveys were carried out in Shannonbridge over the last 8 years and the results are displayed in Table 3. Not only are all the measurements below 400 Bq·m^{-3}, but they are all similar to outdoor radon concentrations commonly measured in Ireland. As such, they are of no radiological significance from the point of view of radon occupational exposure.

Table 3. Results of passive long-term radon measurements carried out in the Shannonbridge peat-fired power plant and associated effective dose (µSv·y^{-1}); (1) Based on the characteristics of each work practice on site; (2) Employees in the maintenance room spend the whole working year at this location; (3) ICRP 65 [18] dose coefficients and F factor of 0.4 used for the calculations; (4) Calculated assuming a maximum radon concentration of 15 Bq·m^{-3} in the boiler room

Location	**Measurement period**	**Radon concentration (Bq·m^{-3})**	**Assumed exposure duration (h·y^{-1})** (1)	**Effective dose from radon inhalation (µSv·y^{-1})** (3)
Maintenance room	02/1995 to 05/1996	17	2000 (2)	110
Conference room	02/1995 to 05/1996	33	20	2
Tippler area	12/2002 to 03/2003	11	100	3
Bunker	12/2002 to 03/2003	12	100	4
Control room in bunker	12/2002 to 03/2003	10	0 (unoccupied)	0
Boiler 1	12/2002 to 03/2003	10	680	32 (4)
Boiler 2	12/2002 to 03/2003	15		

4.4. Ambient gamma dose rate measurements

The locations of the measurements carried out are displayed on Figure 1 and the results are shown in Table 4.

Table 4. Ambient gamma dose rate measurements at the Shannonbridge peat-fired power plant and associated effective dose (µSv·y^{-1}); (1) [15]; (2) Based on the characteristics of each work practice on site

Locations	**Dose rate recorded (µSv·h^{-1})**		**Assumed exposure duration (h·y^{-1})** (2)	**Effective dose (µSv·y^{-1})**
	PDR1	GM6-80		
Tippler area	0.06	0.06	100	6
Bunker area	0.08	0.06	100	8
Boiler 1 – Bottom ash area	0.12	0.07	340	41
Boiler 2 – Bottom ash area	0.18	0.07	340	61
Bottom ash pile (inactive disposal area)	0.08	0.07	50	4
Bottom ash pile (active disposal area)	0.08	0.07	500	40
Wet ash pond	0.13	0.06	400	52
Control measurement (outside plant)	0.13	0.07	2000	260
Irish average (1)	0.03 (absorbed dose rate in air 33 nGy·h^{-1})		2000	66

The values given by the two dose rate meters are in good agreement and range from 0.06 to 0.18 µSv·h^{-1}. They are not significantly different from the ambient gamma dose rate recorded outside the perimeter of the plant and used as a control measurement of the natural background (0.07 – 0.13 µSv·h^{-1}). More than likely, the readings given by the GM6-80 (0.07 µSv·h^{-1} on average) give a better idea of the real situation as these are integrated counts over 20 minutes instead of instantaneous values given by the PDR1 (0.10 µSv·h^{-1} on average). In Ireland, the average absorbed dose rate in air is 33 nGy·h^{-1}, with a range of 2 to 110 nGy·h^{-1} [15]. Using a conversion factor of 1 Sv·Gy^{-1} [7], it leads to an average effective dose for adults of 0.03 µSv·h^{-1} (range of 2×10^{-3} to 0.11 µSv·h^{-1}). Therefore, the dose rates measured in Shannonbridge are within the range of natural variations, although clearly in the upper part of this range.

5. Discussion

5.1. Peat harvesting

Radiation dose arising from exposure to external gamma radiation of terrestrial origin for workers involved in the harvesting of the peat all year round should be lower than the natural background value. It should also be lower than the dose arising from a ‘normal’ outdoor work activity. This is because activity concentrations measured in the raw peat are lower than in average Irish soils. Harvesting is carried out in open-air by machineries and workers are wearing facial masks and protective clothing to protect them from any windborne peat dust. Radiation dose arising from inhalation of peat dust is therefore minimized.

5.2. Enrichment factors

Enrichment factors calculated in this study are not significant compared to other published values [16]. It is recognised that the levels of enhancement of radionuclide concentrations in ash are very variable. This is mostly due to differences in the raw peat, the type of furnace, the combustion temperature and the operational characteristics of the plant [6]. For example, the temperature in the furnace at Shannonbridge is 1000-1100˚C, which is lower than the combustion temperature of 1250-1350˚C quoted in Mustonen and Jantunen [4].

5.3. Inhalation of airborne peat dust in the bunker

Radiological assessments usually refer to the inhalation of contaminated dust as a major pathway by which workers dealing with NORM are likely to be receiving the largest radiation dose. Calculations were undertaken to determine the committed effective dose arising from inhalation of peat dust likely to be received by an employee in the bunker over the working year. A sample of airborne peat dust that had settled on shelving adjacent to the personal sampling pump was collected and analyzed by gamma spectrometry. This enabled the amount and type of radionuclides likely to be in the airborne peat dust to be determined (Table 1, dust in bunker). The committed effective dose from inhalation of peat dust was calculated using the formula:

$$D_{inh} = t_{\exp} \times V \times \sum \left(g_{inh,r} \times c_r \right) \qquad (2)$$

where t_{exp} is the exposure duration (assumed to be 100 hours over the year), V is the breathing rate (1.18 $m^3 \cdot h^{-1}$ for light work, [6]), $g_{inh,r}$ is the inhalation dose factor for the nuclide r (in $Sv \cdot Bq^{-1}$, [19]) and c_r is the ambient air activity concentration for the radionuclide r ($Bq \cdot m^{-3}$). Results of the calculations are shown in Table 5. The committed effective dose resulting from inhalation of peat dust in the bunker over the working year is less than 1 µSv (0.89 $\mu Sv \cdot y^{-}1$) and therefore insignificant. It should be noted that this dose is the maximum likely to be received by any worker as it was calculated assuming no PPE.

Table 5. Committed effective dose from inhalation of airborne peat dust in the bunker area; (1) See Table 1. ^{210}Pb and ^{210}Po are assumed to be in equilibrium; (2) Dust concentration is equal to *A* / *v* where *A* is the amount of peat dust breathed in during an 8-hour shift (23.78 mg) and *v* is the flow rate of the pump (2 l·min) multiplied by the duration of the experiment (465 min) and divided by 1000; (3) Ambient air activity concentration for the radionuclide r (Bq·m-3) is the product of the assumed activity concentration by the dust concentration; (4) Inhalation dose factor for the nuclide r (AMAD 5 µm, [19])

Radionuclide r	^{226}Ra	^{210}Pb	^{210}Po	^{228}Ra	^{228}Th	Unit
Assumed activity concentrations in peat dust (1)	15	50	50	1	1	$Bq\cdot kg^{-1}$
Dust concentration (2)	25.6					$mg\cdot m^{-3}$
c_r (3)	3.8×10^{-4}	12.8×10^{-4}	12.8×10^{-4}	2.6×10^{-5}	2.56×10^{-5}	$Bq\cdot m^{-3}$
$g_{inh,r}$ (4)	1.2×10^{-5}	1.1×10^{-6}	7.1×10^{-7}	1.7×10^{-6}	2.3×10^{-5}	$Sv\cdot Bq^{-1}$
$g_{inh,r} \times c_r$	4.6×10^{-9}	1.4×10^{-9}	9.1×10^{-10}	4.3×10^{-11}	5.9×10^{-10}	$Sv\cdot m^{-3}$
$\sum g_{inh,r} \times c_r$	7.5×10^{-9}					$Sv\cdot m^{-3}$
Exposure duration t_{exp}	100					$h\cdot y^{-1}$
Breathing rate V	1.18					$m^3\cdot h^{-1}$
$\boldsymbol{D_{inh}}$	**0.89**					**µSv·y^{-1}**

5.4. Radon and radon daughters inhalation

Another significant exposure pathway in workplaces where NORM materials are processed is radon inhalation from storage of important quantities of materials in a warehouse [20]. In our case, it could be possible that the peat (bunker area) and peat ash (bottom ash in the boiler area) stored onsite may contribute significantly to the total occupational exposure due to the quantities involved. Another exposure situation which would arise from large quantities of fly ash stored in an enclosed space would be the cleaning of the grit arrestors or the freeing of blockages in the hoppers. The radiological assessment of these work activities was not carried out as they did not occur at the time of our site visits. This maintenance work would arise 3 times in a year approximately, would take up to 5 days to be completed and would be undertaken under very strict conditions (obligation to wear respiratory equipment, over clothing, gloves, etc) using water sprays for dust suppression. The annual effective dose from inhalation of radon and radon daughters at different locations throughout the plant (Figure 1) was calculated for the levels measured across the plant and by taking into account the exposure duration at each location (Table 3). The highest dose calculated would be received in the maintenance room and is 0.11 mSv·y^{-1}, which is only 10% of the annual limit under S.I. 125 of 2000.

5.5. Exposure to external gamma radiation in the plant and on the landfill sites

The annual effective dose arising from exposure to external gamma radiation was calculated on the basis of the maximum dose rate measured at each location in the plant (Figure 1) multiplied by the exposure duration at each location (Table 4), They are all below the annual effective dose calculated for the control site (Shannonbridge church).

6. Conclusions

Table 6 summarises all the doses arising from different pathways calculated in the framework of this study.

Table 6. Occupational radiation doses calculated for workers at Shannonbridge; (1) calculated assuming outdoor radon concentration of 10 Bq·m^{-3} [7] and a F factor of 0.8 (instead of 0.4 indoors)

Location / exposure duration	**Dust inhalation (μSv)**	**Inhalation of radon and progeny (μSv)**	**External gamma irradiation (μSv)**	**TOTAL (μSv)**
Tippler / 100 h·y^{-1}		3	6	9
Bunker area / 100 h·y^{-1}	0.89	4	8	13
Boiler area / 680 h·y^{-1}		32	102	134
Bottom ash pile (inactive) / 50 h·y^{-1}		3 (1)	4	7
Bottom ash pile (active) / 500 h·y^{-1}		32 (1)	40	72
Wet ash pond / 400 h·y^{-1}		25 (1)	52	77
Maintenance duties / 170 h·y^{-1}	undetermined	undetermined	undetermined	undetermined
TOTAL / 2000 h·y^{-1}				**312**

The total annual effective dose likely to be received by a worker involved in the processing of the peat and handling of the peat ash in Shannonbridge is approximately 0.3 mSv (312 μSv). The exposure pathways taken into account are the peat dust inhalation in the bunker area, the inhalation of radon and radon progeny and the external gamma irradiation at different locations in the plant.

Therefore, most of the exposure situations where workers are involved on a regular basis are covered, with the exception of maintenance duties like the cleaning of the hoppers and the freeing of blockages in the grit arrestors. These duties are the only ones where workers are directly in contact with the peat fly ash. One would not expect the annual effective dose associated with these duties to be significant as this type of work is always carried out with PPE, is undertaken in wet conditions, occurs non-routinely (3 times in a year) and is usually completed within a week. Another exposure situation not covered in this study is the inhalation of peat ash dust on the landfill sites arising from the generation of windborne ash on the ash pond. However the top layer of the pond, when dried out, usually forms a crust underneath which the ash is trapped. It is therefore unlikely to be wind blown.

References

1. Stationery Office, *Radiological Protection Act, 1991 (Ionising Radiation) Order. Statutory Instrument 125 of 2000*, Department of Public Enterprise, Government Publications Office, Dublin (2000).
2. Council of the European Union, *Basic Safety Standards for the Health Protection of the General Public and Workers Against the Dangers of Ionising Radiation*, Council Directive 96/29/EURATOM, Luxembourg (1996).
3. Madden, J.S., *Radon in dwellings in selected areas of Ireland*, Report RPII-94/3, Radiological Protection Institute of Ireland, Dublin (1994).
4. Mustonen, R., Jantunen, M., *Radioactivity of size fractionated fly-ash emissions from a peat- and oil-fired power plant*. Health Physics, 49:1251-1260, (1985).
5. McAulay, I.R., Department of Physics, Trinity College Dublin. *Unpublished data* (1986-1990)
6. Smith, K.R., Crockett, G.M., Oatway, W.B., Harvey, M.P., Penfold, J.S.S., Mobbs, S.F., *Radiological impact on the UK populations of industries which use or*

produce materials containing enhanced levels of naturally occurring radionuclides: Part I: Coal-fired Electricity Generation, Report NRPB-R327, National Radiological Protection Board, Chilton, Didcot (2001).

7. United Nations Scientific Committee on the Effects of Atomic Radiation, *Sources and Effects of Ionizing Radiation*. Report to the General Assembly, with Scientific Annexes. United Nations, New York (2000).

8. Finch, E.C., *A radiological analysis of peat ash samples supplied by ESB International*, Unpublished report to the Electricity Supply Board, Trinity College, Ireland (1998).

9. Mustonen, R., *Building Materials as sources of indoor exposure to ionising radiation*. Report STUK-A105, Strålsäkerhetscentralen, Helsinki (1992).

10. Von Philipsborn, H., Kuhnast, E., *Gamma spectrometric characterisation of industrially used African and Australian bauxites and their red mud tailings*. Rad. Prot. Dos., 45:741-744, (1992).

11. International Atomic Energy Agency, *Radioactivity in material not requiring regulation for purposes of radiation protection*, Draft Safety Guide DS-161, Safety Standards Series, IAEA, Vienna (2003).

12. European Commission, *Practical use of the concepts of clearance and exemption – Part II Application of the concepts of exemption and clearance to natural radiation sources*. Radiation Protection 122. EC Directorate-General Environment, Luxembourg (2001).

13. Hofmann, J., Leicht, R., Wingender, H.J., Worner, J., *Natural radionuclide concentrations in materials processed in the chemical industry and the related radiological impact*, Report EUR 19264, Nuclear Safety and the Environment, European Commission, Luxembourg (2000).

14. O’Grady, J., *Radioactivity and fertilisers*. Technology Ireland, 24:41-45, (1992).

15. Marsh, D., *Radiation mapping and soil radioactivity in the Republic of Ireland*, MSc. Thesis, Trinity College, National University of Ireland, Dublin (1991).

16. European Commission, *Enhanced radioactivity of building materials*. Radiation Protection 96. EC Directorate-General Environment, Luxembourg (1999).

17. National Authority for Occupational Safety and Health, *Code of Practice for the Safety Health and Welfare at Work (Chemical Agents) Regulations 2001*, Government Publications Office, Dublin (2002).

18. International Commission on Radiological Protection, *Protection against Radon-222 at home and at work*. Publication 65. Annals of the ICRP, 23, No. 2, Pergamon Press, Oxford (1994).

19. International Commission on Radiological Protection, *Dose coefficients for intakes of radionuclides by workers*. Publication 68. Annals of the ICRP, 24, No. 4, Pergamon Press, Oxford (1994).

20. Penfold, J.S.S., Mobbs, S.F., Degrange, J.P., Schneider, T., *Establishment of reference levels for regulatory control of workplaces where materials are processed which contain enhanced levels of naturally-occurring radionuclides*. Radiation Protection 107. EC Directorate-General Environment, Luxembourg (1999).

EXPOSURE FROM AN IGNEOUS PHOSPHATE MINE OPERATION

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INTRODUCTION

The facility under discussion is a South African Open Cast Mine that produces igneous phosphate rock, with intermediate and final products for the domestic and international markets. It provides the following strategic advantages:
Make South Africa self-sufficient from phosphate imports.
Earn foreign currency from the export of the mineral.

Create approximately 2000 direct job opportunities, with associated indirect job opportunities in the Greater Phalaborwa region.

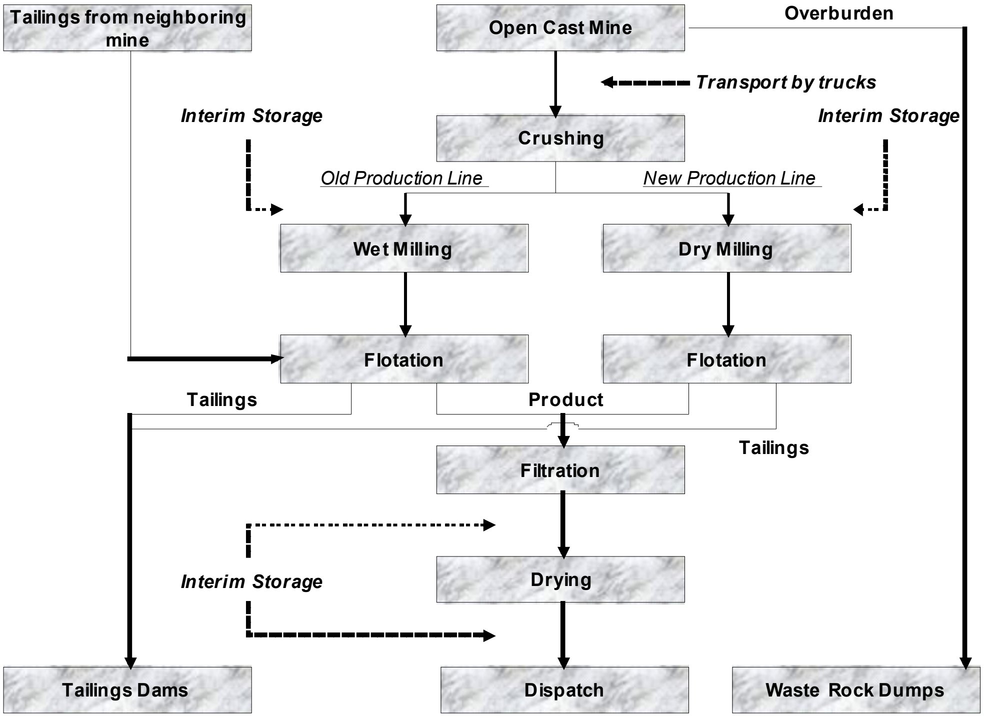
Approximately 3.0 million tons of phosphate rock is produced annually and the product is a finely ground apatite mineral from a coarsely crystalline calcium-fluoride-phosphate compound of magmatic origin.

The mine is located adjacent to the towns of Phalaborwa, Namakgale and Lulekani, bordering on the Kruger National Park in the Limpopo Province.

The company obtained a Nuclear Authorisation in terms of the South African Nuclear Energy Act, No 131 of 1993 in 1993 and has been holder of an authorisation since. It changed in 2002 to a Certificate of Registration, issued under the auspices of the National Nuclear Regulatory Act, No 47 of 1999.

PRODUCTION PROCESS

The following is a simplified diagram of the mining and beneficiation process.



SPECIFIC ACTIVITY

Table 2.2-1 below summarises the known specific activities of the major sources of material involved in the process, e.g. Phosphate Rock and Phosphate Tailings.

Table 3-1: Nuclide specific activity of the process material

Nuclide	Specific Activity (Bq.g^{-1})	
	Phosphate Rock	Tailings
U-238	0.14	0.26
Ra-226	0.14	0.27
Pb-210	0.12	
Th-232	0.47	0.31
Ra-228	0.55	0.33
Th-228	0.55	0.35

ISOTOPES CONSIDERED

The following isotopes were considered in the assessment process.

Table 4-1 Isotopes of the natural decay series used in the calculation of the dose conversion factor

Uranium - Series	Actinium - Series	Thorium – Series
U-238	U-235	Th-232
U-234	Pa-231	Ra-228
Th-230	Ac-227	Th-228
Ra-226	Th-227	Ra-224
Pb-210	Ra-223	Bi-212
Po-210		

The National Nuclear Regulator does not generally require the inclusion of U-235 and daughter isotopes in the assessment process and for the initial screening survey, it was excluded. However, where the gross alpha activity is used for dose determination, it was deemed appropriate to include the Actinium Series when calculating its dose conversion factor as it may have a measurable effect.

METHODOLOGY

Occupational Exposure

Occupational exposure consisted of two pathways for the purpose of this assessment, namely External Exposure from the gamma component and Inhalation [1, 2]. Ingestion was excluded, as it is not a regulatory requirement in South Africa. The external exposure was measured at various locations in a specific section and the doserate at 1 meter used in this assessment process.

Two methods of determining internal dose were used to calculate the occupational dose, one more suitable for screening assessment purposes and the other a more realistic calculation.

Method 1

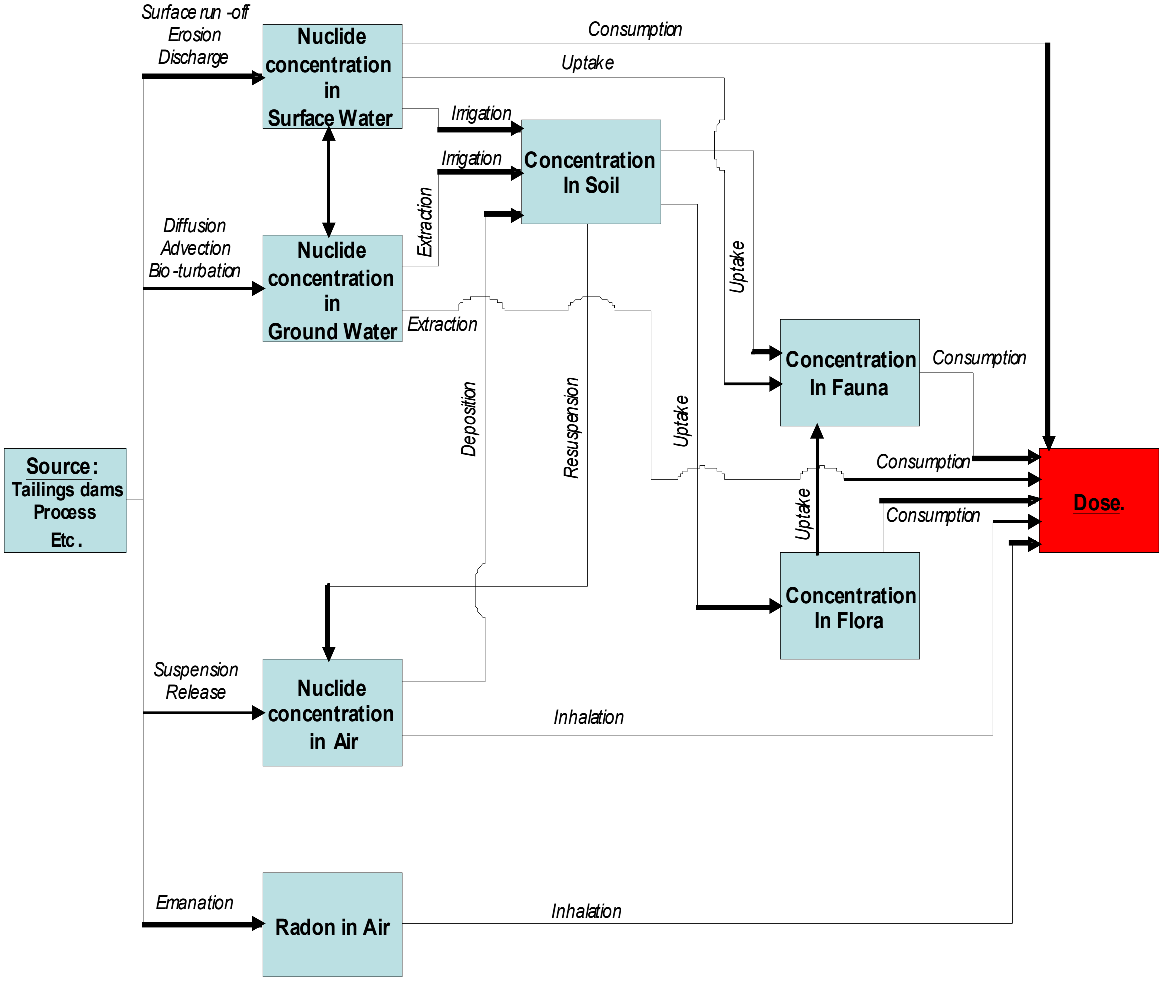
The screening assessment utilized area air concentrations as collected though an Occupational Hygiene program and the average isotope specific activity of phosphate or tailings (See Table 3-1). An occupancy factor of 1 is used, also assuming 250 shifts per year, each lasting 9.5 hours.

Method 2

The assessment was repeated but based on actual measurements in the production areas. This method used gross alpha activity measured on the area air samples collected in the plant and a calculated dose conversion factor for phosphate rock and tailings. (See Table 4-1.)

Public Exposure

The radiological impact of the facility on members of the public was determined with the aid of mathematical models such as described in IAEA Technical Report Series 364 and Safety Report Series 19 [3, 4]. The following diagram is summary of the generic pathways that received consideration in the public assessment process of the company.



The above were then applied to the Phalaborwa facility to determine actual and hypothetical critical groups during the initial risk assessment [4].

Three actual critical groups were identified for the facility. They are a family living in the town of Phalaborwa, a family living in Namakgale, (both to the North and Northeast), and a family living to the South East of the facility. It was assumed that all the age groups were represented in each critical group, although for the purposes of this paper only the Adult exposure is reported.

Table 5.1.2-1: Pathways considered for the actual critical groups

Description	Scenario			Remarks
	1	2	3	
Drinking Water, either from river or groundwater.	-	-	✓	See discussion below.
Vegetables	✓	✓	✓	Fulfil their daily needs.
Fruit	✓	✓		Fulfil their daily needs.
Fish	✓	✓	✓	Fish in the dams on the mine property. (Actual practice.)
Meat	-	✓	✓	Fulfil their daily needs.
Milk	-	✓	✓	Fulfil their daily needs.
Poultry	-	✓	✓	Fulfil their daily needs.
Eggs	-	✓	✓	Fulfil their daily needs.
Cereal	-	✓	✓	Fulfil their daily needs.
Air (Inhalation)	✓	✓	✓	Concentration will vary since the distance between source and receptor, climatic conditions etc, are different.
Radon (Inhalation)	✓	✓	✓	
External Radiation	✓	✓	✓	As a result of deposition.

Drinking water is generally obtained from the local Water Board, a source not affected by the facility. However, for Scenario 3 it was assumed that some water for drinking purposes is extracted from the Selati River or from a borehole.

RESULTS & DISCUSSION

Occupational Exposure

For Method 2, an Inhalation Dose Conversion Factor, using the average nuclide specific activities for phosphate rock and tailings, were calculated to be 1.23E-05 $Sv.\alpha Bq^{-1}$ for Phosphate Rock and 9.63E-06 $Sv.\alpha Bq^{-1}$ for Tailings.

The total dose for the various phosphate production and waste disposal areas is summarised in the following table.

Table 6.1-1: Occupational exposure for the Phosphate Production Areas.

Area	Internal (mSv.a^{-1})		External (µSv.h^{-1})	Total (mSv.a^{-1})	
	Method 1	Method 2		Method 1	Method 2
Mining					
Crushing and Loading	0.25	0	0.22	0.69	0.44
Primary Crushers		0.11	0.22	0.69	0.55
Secondary Crushers		0.11	0.11	0.47	0.34
Tertiary Crushers		0.11	0.11	0.47	0.34
Milling					
Operations	-	0.11	0.20	-	0.51
Workshop	-	0.00	0.19	-	0.38
Flotation					
Copper	0.14	0.00	0.33	0.80	0.67
Phosphate		0.00	0.22	0.58	0.44
Magnetic Separation		0.32	0.33	0.80	0.98
Workshop		0.00	0.21	0.55	0.43
Filtration					
Operations	0.31	0.24	0.21	0.72	0.65
Workshop		0.00	0.22	0.75	0.44
Extension 8					
Crushing	0.26	-	0.20	0.66	-
Conveyors		-	0.24	0.74	-
Milling		-	0.20	0.66	-
Flotation		-	0.19	0.64	-

Area	**Internal (mSv.a^{-1})**		**External (µSv.h^{-1})**	**Total (mSv.a^{-1})**	
	Method 1	**Method 2**		**Method 1**	**Method 2**
Workshop	0.002	-	0.26	0.52	-
Drying & Dispatch					
Operations	0.14	0.32	0.29	0.72	0.90
Workshop	0.02	0.00	0.24	0.50	0.49
Tailings					
Workshops	0	0.08	0.22	0.44	0.52
Research & Development					
Laboratory	-	0.11	0.31	-	0.72
Pilot Plant	-	0.22	0.21	-	0.64

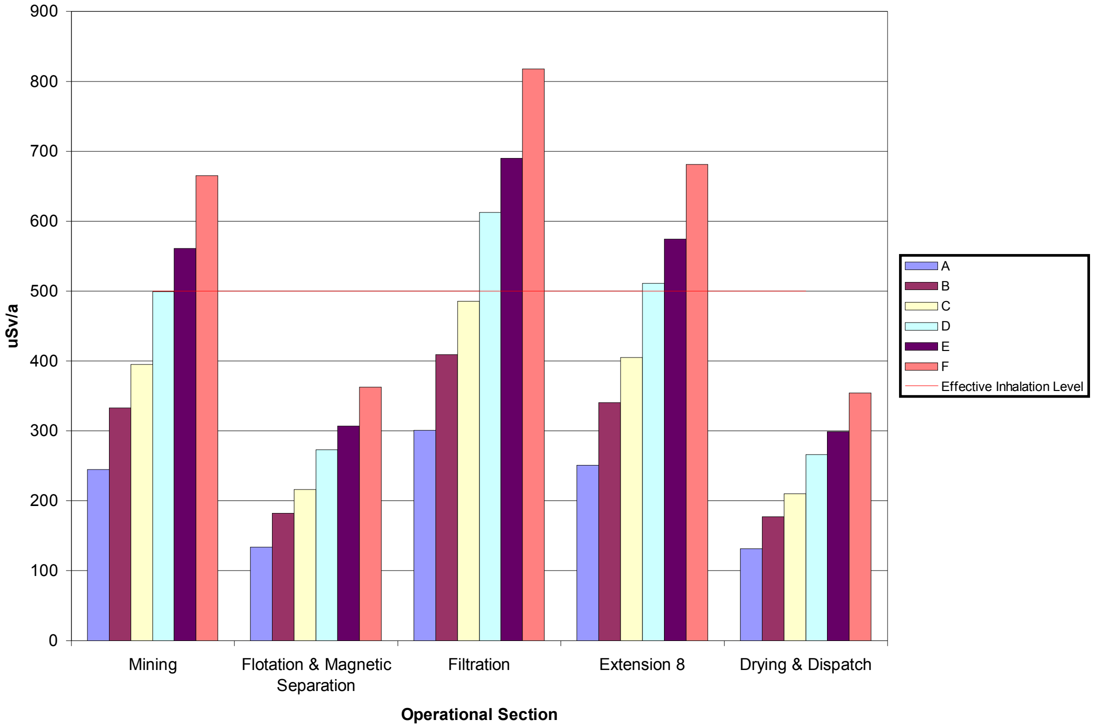
The above shows that occupational exposure at an igneous phosphate mine is less than 1 mSv.a^{-1} and the areas are thus non-controlled. Also apparent is that the resulting dose from the two methods is in the same order of magnitude. The gross alpha activity determination is therefore not really necessary and can be excluded, thus saving on the cost of an initial assessment and assessment time. (Both methods require a nuclide specific activity of the process material, while only Method 2 requires additional radiation measurement.)

However, it is also clear that should the concentration of the material in the air or the specific activity of the material increases, some of the areas may require reclassification from Non-Controlled to Supervised.

Occupational Action Level

Using Method 1, an attempt was made to establish Action Levels for two parameters that may change, namely specific activity and airborne concentration. For the purpose of establishing the activity action levels it is assumed that all the other variables remain the same, with an average gamma doserate of 0.46 mSv.a^{-1}. An internal dose level of 0.5 mSv.a^{-1} is thus set, ensuring the total dose remains less than 1 mSv.a^{-1}.

The following figure represents the effect of an increase in nuclide specific activity on the Inhalation Dose if the concentration in the air remains constant.



A $^{238}U = 0.15$ Bq.g^{-1}, $^{232}Th = 0.5$ Bq.g^{-1}

B $^{238}U = 0.5$ Bq.g^{-1}, $^{232}Th = 0.5$ Bq.g^{-1}

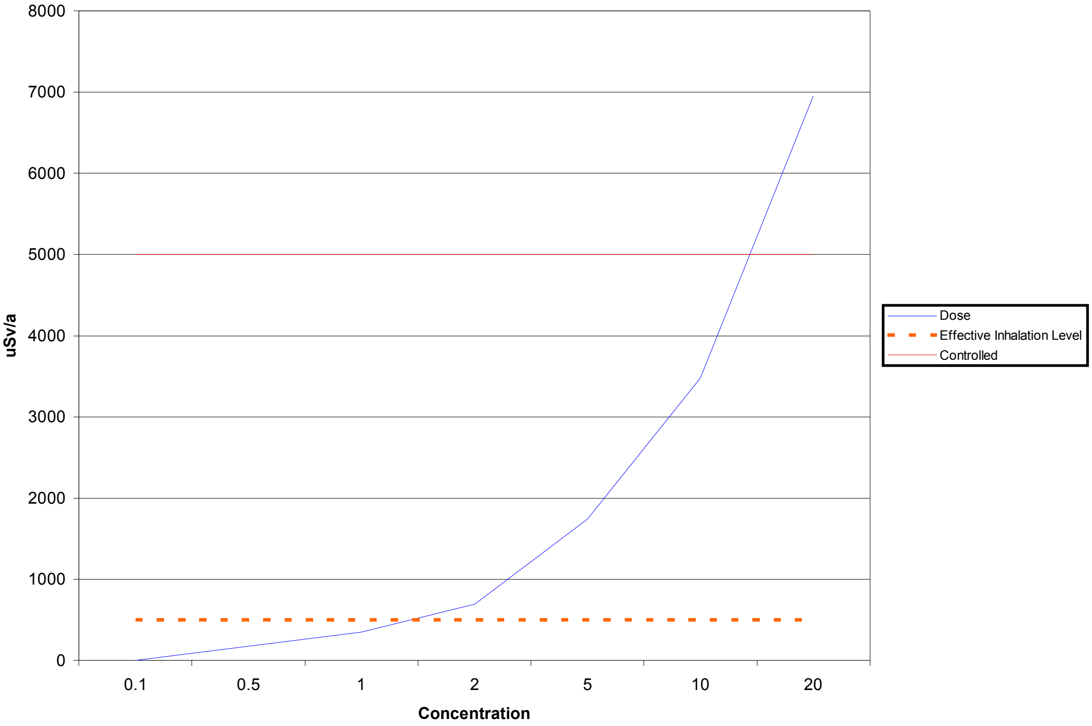
C $^{238}U = 0.75$ Bq.g^{-1}, $^{232}Th = 0.5$ Bq.g^{-1}

D $^{238}U = 0.75$ Bq.g^{-1}, $^{232}Th = 0.75$ Bq.g^{-1}

E $^{238}U = 1$ Bq.g^{-1}, $^{232}Th = 0.75$ Bq.g^{-1}

F $^{238}U = 1$ Bq.g^{-1}, $^{232}Th = 1$ Bq.g^{-1}

Should the specific activity remain the same, but the air concentration increases due to ventilation failure for example, the following is then applicable.



As seen from the above graph, a change in air concentration rapidly leads to unacceptable doses. Should a company therefore wishes to decrease its occupational exposure, focus should be placed on dust control, e.g. extraction, ventilation etc.

Public Exposure

General

The following tables summarises the results of the initial assessment.

Table 6.3.1-1: Dose to actual critical groups

Description	**Scenario 1 (μSv.a^{-1})**	**Scenario 2 (μSv.a^{-1})**	**Scenario 3 (μSv.a^{-1})**
Inhalation: Air	1.56E+01	1.56E+01	3.48E+01
Inhalation: Radon	9.75E-01	9.75E-01	5.90E+00
Water	-	-	2.73E+02
Leafy Vegetables	1.00E-01	1.00E-01	2.20E-01
Root Vegetables	2.72E-01	2.72E-01	5.99E-01
Fruit	1.05E-01	1.05E-01	2.32E-01
Meat	-	2.84E+00	1.55E+01
Milk	-	5.89E-01	9.96E+00
Cereal	-	1.46E-01	3.23E-01
Poultry	-	2.01E-01	4.11E-01
Eggs	-	6.70E-02	1.50E-01
External: Air	5.19E-07	5.19E-07	1.15E-06
External: Soil	4.46E-03	4.46E-03	9.82E-03
Total	**1.71E+01**	**2.09E+01**	**3.41E+02**

Please note that the blocks indicated in bold were not part of the routine monitoring program and the doses were therefore not reviewed.

As stated in Section 2, water was included in Scenario 3 although it is highly unlikely that it is consumed or used in any manner. The groundwater is naturally very saline due to the geological formations in the area and the water is subsequently not suitable for drinking or irrigation. However, to ensure comprehensiveness, it was assumed that some water is desalinated without removing some of the activity and used for drinking purposes. Utilizing the 2001 measurement results for the applicable boreholes as well as the 2002 and 2003 river water analysis results, the incremental dose was reviewed and presented in the following tables.

Table 6.3.1-2: Background corrected dose from groundwater consumption (2001 measurement results.)

Description	Incremental Dose ($\mu Sv.a^{-1}$)
Wet Season	4.70
Dry Season	1.70

Note that for the purposes of this assessment a MDA value is taken as 0.

Table 6.3.1-3: Background corrected dose from surface water consumption (2002 & 2003 measurement results)

Description	Incremental Dose ($\mu Sv.a^{-1}$)
Wet Season (2002)	14.5
Dry Season (2002)	22.9
Wet Season (2003)	8.98
Dry Season (2003)	11.7

Note that for the purposes of this assessment a MDA value is taken as 0.

Thus, assuming the above doses are typical of the current situation, the total dose for Scenario 3 will decrease by at least 250 $\mu Sv.a^{-1}$, even when ignoring the decreased contribution from the water through the secondary pathways, resulting in a public dose of less than 100 $\mu Sv.a^{-1}$.

Problem Encountered

Initially the South African Regulator required a company to use the Minimum Detectable Activity (MDA) of an isotope for dose calculations if the true activity was not measurable. This however, resulted in doses in excess of 5 $mSv.a^{-1}$ from ingesting fish, a secondary pathway, primarily from Pb-210 and Po-210. Refining the analysis techniques has since proved the initial methodology inappropriate as illustrated by the following table.

Table 6.3.2-1: Background corrected dose from fish consumption (2002 & 2003 measurement results)

Description	Dose	Background Dose	Incremental Dose
	$\mu Sv.a^{-1}$	$\mu Sv.a^{-1}$	$\mu Sv.a^{-1}$
2003 Selati River (Wet Season)	23.1	89.2	0
2003 Recreational Dam (Wet Season)	21.1	89.2	0
2003 Selati River (Dry Season)	33.2	89.2*	0

** A background sample could not be collected due to the low level of the Selati River. The background value obtained during the wet season was used as reference.*

CONCLUSIONS

The occupational dose is less than 1 $mSv.a^{-1}$ for the production areas, resulting in a classification of Non-controlled.

An increase in specific activity to 0.75 $Bq.g^{-1}$ for U-238 or a process material air concentration in excess of 1.5 $mg.m^{-3}$ should receive attention, as the resulting dose will probably exceed 1 $mSv.a^{-1}$, requiring a formal radiation protection program.

The dose to members of the public is less than 250 $\mu Sv.a^{-1}$, thus in compliance with South African legislation.

REFERENCES

[1] RAD/R/004: Report on a Radiological Screening Survey of the Foskor Processing Plant. July 1994.GP de Beer

[2] RAD/R/9523: Revision of Report on a Radiological Screening Survey of the Foskor Processing Plant. September 1995. GP de Beer.

[3] Review of occupational exposure at Foskor – Radiological Risk Assessment. March 2004. AJ vd Westhuizen

[4] IAEA Safety Report Series 19: Generic models for use in assessing the impact of discharges of radioactive substances to the environment, 2001.

[5] IAEA Technical Report Series 364: Handbook of parameter values for the prediction of radionuclide transfer in temperate environments, 1994.

[6] GEA-1372: Radiological Public Hazard Assessment Study for Foskor (Pty) Ltd. JJP Vivier, IE Steyn, JJ van Blerk. (1999)

RAIL TRANSPORT OF IGNEOUS PHOSPHATE ROCK

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SCOPE

This risk assessment evaluates the rail transport of igneous phosphate rock from the Phalaborwa Complex, South Africa, to the harbour in Richards Bay, South Africa. Marine transport and the loading and unloading of ships are not included. It reports on doses likely to be incurred during normal operations by workers as well as members of the public and make some reference to exposures during abnormal conditions. In conclusion, the assessment shall identify areas that require further assessment.

BACKGROUND

The third Research Co-Ordination Meeting on the Development of a Radiological Basis for the Transport Safety Requirements for Low Specific Activity Materials and Surface Contaminated Objects (LSA/SCO) was held in Cape Town, South Africa on the 19th to 23rd of February 2001. It was attended by the Chief Scientific Investigators (CSI) from Brazil, Canada, France, Germany, South Africa and the United Kingdom, with the IAEA acting as Scientific Secretary. In addition to the CSI's, Observers of South Africa and Japan participated. This meeting is part of a Cooperative Research Project (CRP), to investigate an area of concern, specifically the radiation protection basis for the International Atomic Energy Agency (IAEA) transport regulations. Upon completion of the CRP a TECDOC, summarising the work of the CRP, is to be prepared.

A Phosphate Rock and Fertiliser Producer (South Africa) participated under observer status during the event and agreed to repeat the zircon sand study for igneous phosphate rock and phosphoric acid to support the theoretical models although the material is strictly speaking not subject to the requirements of the IAEA Regulations for the safe transport of radioactive materials [1]. This report represents a partial fulfilment of the commitment, evaluating (a) the occupational exposure during the loading of phosphate rock on rail cars, transport and unloading in the harbour (b) public exposure during rail transport and interim storage in silos and (c) give some reference to undesired events, such as spillages as seen from a South African Industry perspective. It uses, where possible, the scenarios described in the transport assessment study done for zircon sand, to allow comparison between the results.

PHOSPHATE INDUSTRY

Introduction

Four nutrients have been identified that are vital for healthy and rapid plant growth. They are nitrogen, phosphorus in the form of phosphate (P_2O_5), potassium (usually as K_2O) and sulphur.

To quote [2]: *"Phosphorus is primarily responsible for all processes in plant life in which energy is stored and utilized. It promotes root growth. It improves the quality of grain and accelerates its ripening."*

Initially, bones were used as the prime source of phosphate, but the discovery of large deposits of phosphate rock overcame the constraints of limited supply. However, these sources contains naturally occurring radionuclides to a varying degree, with the true impact of the industry in terms of the radionuclides content yet to be fully quantified.

Specific Activity

There are two sources of phosphate-bearing material, both containing naturally occurring isotopes and is defined by its origin. The most common source is phosphate of sedimentary origin, accounting for approximately 86% of the world market. The second source is rock from igneous origin and represents the other 14%.

A significant difference between sedimentary phosphates and the igneous material found in the Phalaborwa Complex (South Africa) lies in the difference in specific activity of the natural decay chains. Sedimentary material has higher concentrations of the U-238 decay series and very low concentrations of Th-232 and its daughter isotopes. On the other hand, the Phalaborwa Complex material has much lower concentrations of the U-238 decay series, but with elevated concentrations of Th-232 and its daughters.

Almost all of the South African phosphate rock originates at the Phalaborwa Complex located in the Limpopo Province and the focus of this assessment will thus be of the effect of this material on workers and possibly members of the public.

Table 3.2-1 summarises some of the known nuclide specific activities as average values for the Phalaborwa material.

Table 3.2-1: Nuclide specific activity of phosphate rock

Nuclide	Igneous Origin ($Bq.g^{-1}$)
U-238	0.14
Ra-226	0.14
Pb-210	0.12
Th-232	0.47
Ra-228	0.55
Th-228/Ra-224	0.55

Para 401(b) of IAEA Safety Series ST1 refers to the activity concentration of exempt material as listed in Table 1. For natural uranium and thorium 1 $Bq.g^{-1}$ is the exempt specific activity. Igneous phosphate rock is thus deemed excluded from the requirements of ST1.

Notwithstanding the above, a decision was made to conduct a detailed risk assessment to support the efforts of both the Transport CRP and the industry risk assessment project of the Fertilizer Society of South Africa.

METHODOLOGY

This risk assessment is based on actual measurements where possible and will only refer to modelling or calculated values where no actual measurements are available.

As stated in the Background section, parameters, (such as distance of dwellings from the tracks and speed of the trains), from the zircon sand study is used where possible to allow direct comparison between the results [3].

Scenario Description

A mine in Phalaborwa is the primary supplier of phosphate rock used by the South African Phosphate- and Fertilizer Industry. The material is also exported through the port of Richards Bay, some 1000 kilometres away.

The beneficiated rock is loaded on site and transported via rail to customers or the export harbour. Product ready for dispatch is stored in silos and from the silos loaded directly on to a rail car. Each car is covered with a tarpaulin before leaving the site. During unloading, the car is tipped over at the Discharge Facility, dropping the material onto a conveyor system from where it is moved to its destination. (Extraction hoses are also sometimes used.)

As a result of this process, workers and members of the public may incur a dose from the work activity during normal and possibly abnormal conditions. The basic rail transport from Phalaborwa to Richards Bay via a 1000 kilometre railway line is thus the main focus of this assessment.

Occupational Exposure

Five actual occupational groups were identified in the assessment process for the transport portion between Phalaborwa and the harbour operations in Richards Bay. It is the Loader, Shunter/Train Driver and the Tarper during loading and the Front-end Loader and Discharge Facility Operator during the unloading process. The following table summarises the basic groups and the pathways considered in the assessment process.

Table 4.2-1: Identified critical groups in terms of occupational exposure and the pathways for consideration.

Classification	Category	Pathways	Remarks
Occupational	Loader	Inhalation, Ingestion, External Gamma	Inhalation and External Gamma: Worker carries the equipment for a full shift. Ingestion: Modelled
Occupational	Shunter/Driver	Inhalation, Ingestion, External Gamma	Inhalation and External Gamma: Worker carries the equipment for a full shift. Ingestion: Modelled
Occupational	Tarpaulin Worker	Inhalation, Ingestion, External Gamma	Inhalation and External Gamma: Worker carries the equipment for a full shift. Ingestion: Modelled
Occupational	Front-end Loader Driver	Inhalation, Ingestion, External Gamma	Inhalation and External Gamma: Worker carries the equipment for a full shift. Ingestion: Modelled
Occupational	Discharge Facility Operator	Inhalation, Ingestion, External Gamma	Inhalation and External Gamma: Worker carries the equipment for a full shift. Ingestion: Modelled

Public Exposure

The public exposure is as follows, referring to the public exposure routes identified in the zircon risk assessment study [3]:

- Public Scenario 1: Member of the public waiting at a rail crossing while the train passes
- Public Scenario 2: Houses en route

- Public Scenario 3: Person sitting against a silo filled with phosphate rock.

The following table summarises the various scenarios and pathways considered for the public impact assessment.

Table 4.3-1: Public exposure scenarios and applicable pathways considered and assessed.

Classification	Category	Pathways	Remarks
Public Scenario 1	Car occupant at a rail crossing.	External Gamma	External Gamma Direct measurement from stop at rail crossing as train passes.
Public Scenario 2*	Occupant of home situated next to the railway line	External Gamma, Inhalation	External Gamma Calculate from exposure to driver of vehicle at rail crossing. Inhalation External measurement from ambient monitors upon completion of dedicated Discharge Facility.
Public Scenario 3	Fisherman sitting against a silo.	External Gamma	External Gamma Contact dose rate measurement of a silo.

* *Public Scenario 2 allow for several variations, as the train travel trough rural, suburban and urban area. However, the most restrictive was considered in the initial assessment.*

A typical train of phosphate rock is approximately 840 meters long. The primary route for this material in South Africa is the one between Phalaborwa and Richards Bay and approximately 700 shipments per year travel on this trajectory. Therefore a member of the public living next to the line is exposed 700 times per year, while it was assumed to be highly unlikely that a member of the public will encounter a phosphate rock train at a crossing more than once per year. However, in view of the zircon transport risk assessment a further variation is assumed, whereby a mother is taking her child to school and wait at a rail crossing at least once per day during the school year, e.g. 250 days per year.

Isotopes Considered

The following radioisotopes contribute almost all of the inhalation and ingested doses and were considered in the assessment.

Table 4.4-1: Isotopes of the natural decay series used in the calculations

Uranium	U-235	Thorium
U-238	U-235	Th-232
U-234	Pa-231	Ra-228
Th-230	Ac-227	Th-228
Ra-226	Th-227	Ra-224
Pb-210	Ra-223	Bi-212
Po-210		

Note: *The National Nuclear Regulator of South Africa does not require the inclusion of U-235 and daughter isotopes in the assessment process. (See LG-1032 [4]) It is included in this document to ensure comprehensiveness.*

Background

Background plays a significant role with the loading of the material as the loading site is partially situated on the igneous ore body. In addition, the loading area is surrounded by sources other than normal background. A decision was therefore made to measure the gamma doserate background for occupational exposure inside the Safety, Health, Environment & Quality buildings at the facility in Phalaborwa as it is less than a hundred meters away from the loading area, thus similar background, but with negligible contribution from the process. The background values are conservative as the shielding effect of the floors is ignored.

The background for the public dose calculations was measured in town and away from the main background source, the igneous ore body. This allows for some conservatism when doing the public exposure assessment.

Incidents

Phosphate rock is only transported by rail in South Africa and thus incidents can only be divided into two broad categories, namely a spillage (the worst being a derailment) and a fire involving the rail cars carrying the rock phosphate. There are thus two worker categories, that of a fireman and the worker responsible for the site remediation after a derailment. The pathways of interest for both are external exposure, inhalation and ingestion. The value of the parameters, include inhalation rate, concentration of respirable dust and the period for exposure however, differ.

An incident assessment for igneous and sedimentary phosphate rock, phosphoric acid and phosphogypsum was conducted and submitted as dissertation to the University of the Witwatersrand, South Africa [5] and the findings of this document will be reported. (The document is under review and should be available in 2004.)

RESULTS

Normal Operating Conditions

Occupational Exposure

Dose Conversion Factor

The inhalation and ingestion dose conversion factor, using the average nuclide specific activities as given in Section 3, are given below.

Table 5.1.1.1-1: Occupational dose conversion factors for phosphate rock

Description	Dose Conversion Factor [Sv.αBq^{-1}]
Inhalation: Igneous Phosphate Rock	1.23E-05 Sv.αBq^{-1}
Ingestion: Igneous Phosphate Rock	2.68E-07 Sv.αBq^{-1}

Background

The background, using the electronic dosimeters measured inside buildings on-site, is presented in the table below.

Table 5.1.1.2-1: Background measurements used for the occupational risk assessment.

Description	Average (μSv/shift)	Standard Deviation (μSv/shift)
Background measurement on site, approximately 100 meters from the loading areas.	2.0	0.05

Total Dose

Three sets of samples, representing the unloading/movement of the rail cars, were taken while one set for workers associated with the Discharge Facility only. The samples were collected during January and February of 2002 at intervals of 1 week. Phalaborwa is a much drier area than Richards Bay, thus representing a very conservative approach when using the results to assess similar actions in Richards Bay.

A summary of the occupational exposure is given in the table below. The results of an assessment that formed part of Foskor's occupational risk assessment, conducted in 1995, are included for comparison [6,7].

Table 5.1.1.3-1: Occupational dose

Category	2002 Assessment					1995 Assessment Results
	Ingestion Dose	Inhalation Dose	External Dose	Dose	Average Dose per Category	
	(μSv.a^{-1})	(μSv.shift^{-1})	(μSv.shift^{-1})	(μSv/a)	(μSv/a)	
Loader	47.0	0	0.01	49.5	201.4	360
		1.293	0.15	407.7		
		0	0.40	147.9		
Shunter	47.0	0	0	47.0	163.0	
		0	0	47.0		
		1.293	0.10	395.2		
Tarpaulin Worker	47.0	0	0.20	97.0	171.4	
		0	0	47.0		
		1.293	0	370.2		
F/end Loader	47.0	0	0	47.0	47.0	
Tip Operator	47.0	0	0	47.0	47.0	

Public Exposure

Public exposure is primarily from external gamma irradiation as the tarpaulin cover prevents resuspension of the material during transport, making it available for inhalation. Direct measurements were carried out at a rail crossing of a train passing, but the natural background in that area was too high for a meaningful correction. (The loading area is on top of the ore body.)

Background

Background was measured in town, thus ensuring a conservative dose estimate. The dose rate measurements were integrated values, each obtained over a period of 60 seconds. In each instance the detector was held at a level approximately equal to that of a person sitting in a car. The background, using the electronic dosimeters measured inside buildings on-site, is presented in the table below.

Table 5.1.2.1-1: Background measurements used for the public risk assessment.

Description	Average (μSv/h)	Standard Deviation (μSv/h)
Background measurement in town, approximately 11 kilometres from the facility.	0.218	0.07

At a Rail Crossing

The speed of the train, and corresponding dose, was difficult to determine, as it tends to be stop-start. A range of doses for various speeds were calculated and the results, taking cognisance of the above, is given below.

Table 5.1.2.2-1: Dose to member of the public at a rail crossing

Train Speed ($Km.h^{-1}$)	Dose ($\mu Sv.a^{-1}$)
1	0.11
5	0.02
10	0.01
20	0.006
50	0.002

House near a Railway Line

Table 5.1.2.3-1: Dose to member of the public living in house close to the railway line

Train Speed ($Km.h^{-1}$)	Dose ($\mu Sv.a^{-1}$)
1	77.6
5	15.5
10	7.8
20	3.9
50	1.6

Person sitting against a Silo

Seven measurements were taken on a filled silo in Phalaborwa. Silos are typically constructed from concrete.

The measurements were taken on contact at various heights with the majority of the measurements taken on top of the silo where the concrete is least thick. Each measurement was integrated over a period of 1 minute. The average value was 0.20 $\mu Sv.h^{-1}$. Since the background is 0.22 ± 0.07 $\mu Sv.h^{-1}$ it was concluded that public exposure from a silo is negligible.

Discharge Facility Operations

Public exposure is calculated using generic models given as guidance by the International Atomic Energy Agency [8]. However, these values have not been confirmed by actual measurement and the methodology excluded from this report.

Nevertheless, a summary of the calculated values is presented in the following table.

Table 5.1.2.5-1: Summary of estimated annual doses to members of the public from the Discharge Facility Operations.

Age Group (Years)	Annual Dose (μSv.a^{-1})
0 – 2	6.95E-01
2 – 7	7.49E-01
7 – 12	8.88E-01
12 – 17	1.02E+00
Adult	1.03E+00

Thus, parameters requiring attention for future iterations are the following:

Identification of a monitoring point to represent the critical group.

Discharge rate (Bq.s^{-1}) of the source.

Incidents

The dose assessments of incidents involving phosphate-bearing material were calculated as part of a Masters dissertation titled: “A Radiological Assessment of Some Sectors of the Phosphate Industry” [5]. A summary of the occupational dose for a worker responsible for site remediation after a spillage or to fireman during an emergency situation that involved phosphate-bearing material is given below.

Table 5.2-1: Occupational exposure during incidents.

Description	External Exposure (μSv)	Inhalation (μSv)		Secondary Ingestion (μSv)	Total Exposure (μSv)	
		Without*	With*		Without	With
Worker during site remediation.	0.72	1.80	0.36	0.17	2.69	1.25
Fireman during fire.	0.09	-	1.69	0.02	-	1.80

**With or without respiratory protection.*

DISCUSSION

IAEA Safety Series ST 1 sets safety standards to ensure acceptable and appropriate controls to restrict the risks associated with the transport of radioactive materials [1]. The regulations apply to radioactive materials, with some exclusion, for example for natural materials and ores.

> *"Para 107. The Regulations do not apply to:*
> *(3) natural material and ores containing naturally occurring radionuclides which are not intended to be processed for use of those radionuclides provided the activity concentration of the material does not exceed 10 times the values specified in paras 401 – 406."*

Occupational Exposure

This assessment focused on the loading, unloading and intermediate rail transport of igneous phosphate rock from the Phalaborwa Complex (South Africa). Not included are marine and river transportation. Phosphate rock is only transported in bulk, thus road or air transport is not applicable. Five categories of occupational exposure were identified. They are the Loader, Shunter/Driver, Tarper, Front-end Loader Operator, and the Discharge Facility Operator.

The maximum occupational dose ranging from 47 – 360 μSv.a^{-1} and the operations are thus classified as non-controlled.

Public Exposure

Exposure to undisputed members of the public during transport is limited to external gamma dose, although the loading and unloading may introduce an inhalation component.

Direct gamma doserates in a sufficiently low background area were problematic and an off-site measurement was used for background correction. This introduced additional conservatism as the incremental gamma dose measured from a rail car passing include the higher, on-site background. (It should be remembered that the Phalaborwa facility is build on top of the ore body.)

The distance from the source was approximately five (5)-meters and although representative of a person waiting at a rail crossing, it is very conservative for a housing scenario. Houses are usually at a distance more than ten (10)-meters from the track and the walls allow for some shielding from the direct gamma photons. Nevertheless, in the South African environment some illegal and informal settlement may occur close to the line and such occupancy thus corresponds with the person waiting at a rail crossing.

Doses are less than 80 μSv.a^{-1} for the most exposed critical group, e.g. a person living in a house ~ 5 meters from the line where a full ore train travelling 1 km.h^{-1} passes twice per day. The results reported are thus very conservative and indications are that direct gamma measurements will not be statistically detectable above normal background.

Inadvertent Events

The effects of inadvertent events were modelled as part of a dissertation. Occupational dose for a person responsible for site remediation or the emergency worker during an event, were found to be less than 10 μSv.a^{-1} and outside the scope of regulatory control.

Hypothetical Group: Discharge

A hypothetical critical group was identified e.g. members of the public occupying a dwelling close to a Discharge Facility. The dose to most critically exposed public group, even using a pessimistic model, is less than 10 μSv.a^{-1} and will probably be excluded from regulatory control. However, it must be noted that the assumptions used in this assessment were based on the area characteristics of the coastal environment of Richards Bay, South Africa and the modelled values have not been confirmed through actual monitoring. Characteristics of other facilities, for example inland facilities, may differ so significantly that it would require a site-specific monitoring program to accurately quantify the dose.

CONCLUSIONS

The IAEA transport regulations do not apply to Igneous Phosphate Rock, but other drivers persuaded for the continuation of the risk assessment.

Occupational exposure for the most exposed individual does not exceed 360 μSv.a^{-1} for normal operational conditions and is less than 10 μSv per inadvertent event.

Public exposures are indistinguishable from or barely above background.

RECOMMENDATIONS

Complete the transport assessment of igneous phosphate rock as to include the following:

- Loading of ship
- Ship Transport
- Unloading of ship
- Public exposure from airborne contaminants released by Discharge Facility Operations.

Parameters requiring attention for future iterations when assessing the releases from the Discharge Facility Operations are the following:

- Identification of a monitoring point to represent the critical group.
- Verification of the modelling results through measurement.
- Discharge rate (Bq.s^{-1}) of the source.

Comparison between barge and ocean transport should be made to determine if the study should be expanded to include the barge scenario.

Repeat full assessment for sedimentary phosphate rock.

Repeat full assessment for transport of phosphogypsum, phosphoric acid and fertilisers of both igneous and sedimentary origin.

REFERENCES

[1] International Atomic Energy Agency Safety Series TS-R-1 (ST 1, Revised): Regulations for the safe transport of radioactive materials. (1996)

[2] United Nations Environment Program and International Fertilizer Industry Association. *The Fertilizer Industry, World Supplies and the Environment*. (December 1998.)

[3] JH Selby, W Enslin, J Slabbert, R Strydom. Risk assessment of the bulk transport of zircon sand. (2002)

[4] Council for Nuclear Safety (South Africa) LG-1032: Guideline on the assessment of radiation hazards to members of the public from mining and minerals processing facilities. Revision 0. (1997).

[5] AJ van der Westhuizen. A Radiological Assessment of some sectors of the Phosphate Industry. University of the Witwatersrand, South Africa. (July 2003 - Pending)

[6] GP de Beer. Report on a radiological screening survey of the Foskor Processing Plants. AEC Report RAD/R/004. (July 1994)

[7] GP de Beer. Revision of report on a radiological screening survey of the Foskor Processing Plants. AEC Report RAD/R/9523. (September 1995)

[8] International Atomic Energy Agency Safety Report Series No. 19: Generic models for use in assessing the impact of discharges of radioactive substances to the environment. (2001)

NORM IN BUILDING MATERIALS

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Most of their time people in highly developed countries spend inside. For this reason it is very important to know how favorable the situation is inside their premises.

It is very well known that mainly people are irradiated by natural sources of ionizing irradiations which exist in all building materials. Their amount varies greatly: from the lowest-background to the amount which 200 times and more exceeds their background. In industrial countries this problem is being very seriously considered.

In the FSU such investigations were conducted in all its constituent republics. Average value of a specific activity (C_{ef}) of natural radionuclides in the building materials utilized in Azerbaijan was 69 Bq/kg. It was 2 times lower than in some other republics.

Special investigations of radionuclide standardization of building materials were conducted in Azerbaijan under the supervision of F.G.Aliev with the participation of M.B. Brodskaya, F.A. Aslanov et al. As a result in 1993 there were prepared “Provisional republic standards of radioactivity of building materials” (PCH 31-93 Gosstroy Az.R). Not with standing their data and provisional character they are still used as standards for the building materials. During this time there appeared cements of new brands and new brands of imported building materials which are manufactured of hazardous toxic waste. “Gosstroy” (State Construction Administration) should systematically conduct radiometric monitoring and to strong then requirements to quality of the building materials.

Such details of interior like suspended ceilings, plastic frames etc. should be made of materials absolutely free of radioactive materials. If such exist it demonstrates improper quality of the initial material and ready product.

One of the main methods of control for the state of the initial material and the ready product is gamma-spectrometric analysis. We can illustrate this by results of gamma-spectrometric analysis of the building materials which was carried out in “Radiometry” laboratory in Geology Institute of ANAS.

Given below is table 1 demonstrating results of gamma-spectrometric examination of the suspended ceilings.

According to the Standard of Radioactive Safety 76/87 (SRS 76/87) C_{ef} of natural radionuclides in the building materials should not exceed 370 Bq/kg ($C_{ef} \leq 370$ Bq/kg).

$$C_{эф} = C_{Ra} + 1{,}31\ C_{Th} + 0{,}085\ C_{K} \leq 370\ \text{Bq/kg} \quad (1)$$

Table 1. C_{ef} and amount of radioactive elements in the suspended ceilings

№	C_{ef}, Bq/kg	Amount of radioactive elements, Bq/kg		
		U (Ra)	Th	K
1	0	0	0	0
2	0	0	0	0
3	2,53	2,53	0	0
4	2,93	2,93	0	0
5	5,06	5,06	0	0
6	8,72	6,01	0	34,50
7	74,60	44,59	0	382,77
8	82,31	51,97	0	387,03
9	273,09	270	0	36,86
10	283,63	279	0	34,54
11	386,72	386	0	4,01
12	402,44	399	0	39,33
13	415,15	401	0	173,19
14	417,37	417	0	0
15	424,03	421	0	12,51
16	426,1	424	0	15,28
17	447,98	447	0	0
18	445,93	445	0	9,83
19	456,20	452	0	47,89

The table demonstrates that in the most of the samples of the suspended ceilings the C_{ef} exceeds the standard just at account of the increased amount of radium in materials the suspended ceilings are made of. Radium is a source of radioactive gas radon which is human health hazard. According to the data of examination these ceilings have a high ratio of emanation strengthening the risk of irradiation. There exist ceilings free of radioactive elements. This shows that gamma-spectrometric analysis may help choose radioactive safe ceilings. Fig.1 presents spectrograms of clean ceilings and ceilings contaminated by radioactive elements.

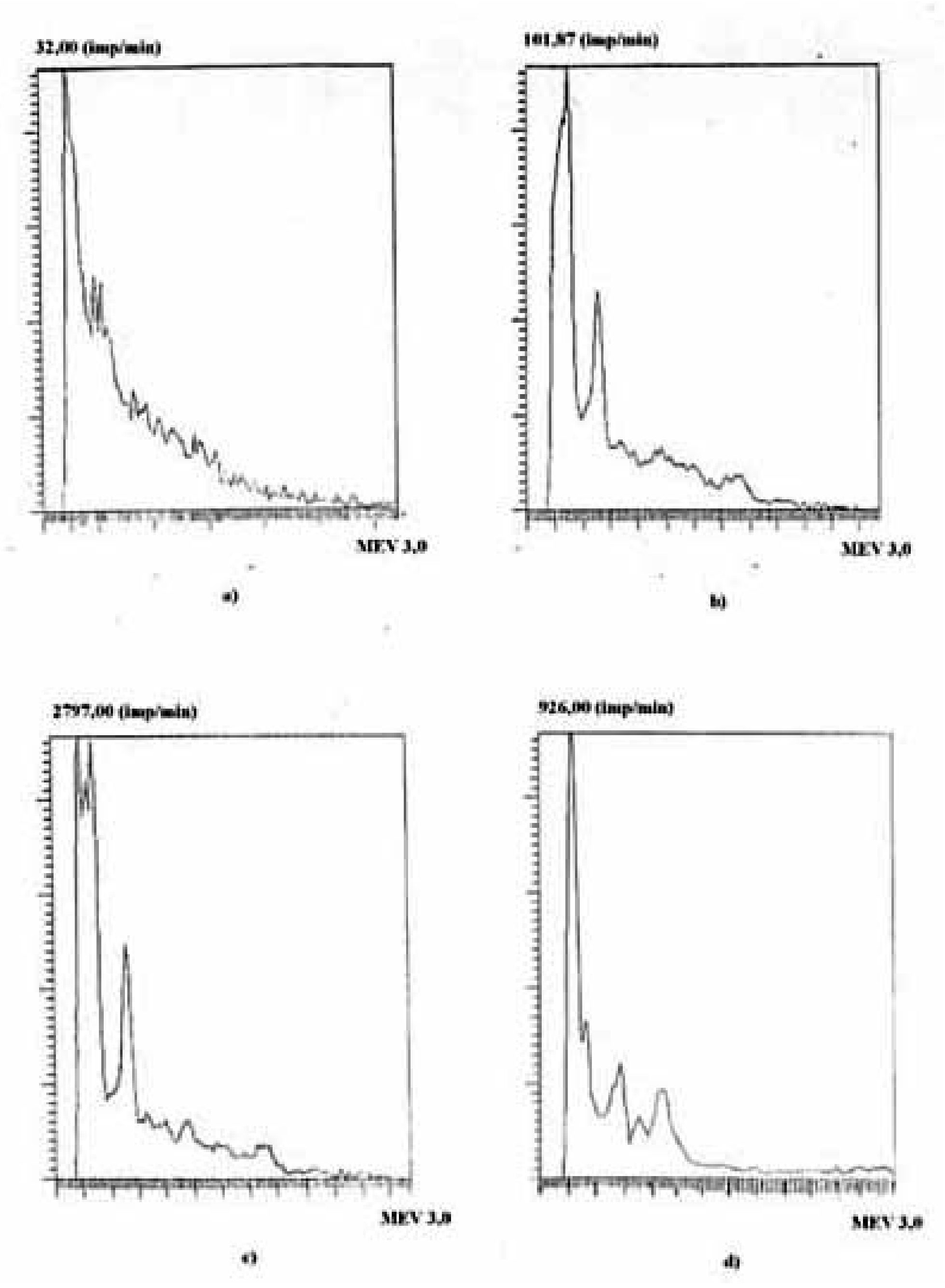

Fig. 1 Spectrograms of building materials:

a) suspended ceiling with normal content of radioelements;

b) suspended ceiling with high content of radioelements;

c) brick with high content of radioelements;

d) asbeetos pipes polluted by radioelements.

Table 2 presents results of gamma-spectrometric examination of bricks. It shows that radioactivity of bricks varies greatly. The bricks being made of natural materials containing natural radioactive elements they always contain uranium, thorium and potassium. During the burning of the bricks concentration of radioactive elements grows. The amount of potassium in the bricks is always increased because they are made of clay containing uranium and thorium. The bricks made of artificial materials with the increased amount of radioactive elements are absolutely useless for the construction of dwellings and public buildings.

Thus, bricks made of vinofiline and industrial waste contain a high amount of uranium and thorium and this makes the situation more hazardous. These bricks can be used during the construction of pipe-lines beyond districts. Fig. 1 demonstrates gamma-spectrums of bricks with a high amount of thorium.

Table 2 demonstrates results of gamma-spectrometric examination of bricks.

Table 2. C_{ef} and amount of radioactive elements in bricks

№	Name	Activity, Bq/kg	Amount of radioactive elements, Bq/kg		
			U (Ra)	Th	K
1	Pink brick	36,29	14,49	2,85	230,35
2	“Elbrus» brick	55,88	17,54	0	488,99
3	Red brick (Zabrat)	75,49	24,18	10,61	477,04
4	Brick (Geokchai)	82,19	41,77	5,84	417,86
5	Dight-grey brick	86,87	35,11	13,92	427,60
6	Red brick	92,97	28,95	21,63	455,08
7	Light brick (Iran)	105,68	70,65	0	446,85
8	Brick (Salyany)	107,12	25,98	21,30	679,00
9	Brick (Ali-Bayramly)	112,79	50,79	9,27	635,85
10	Red brick (Zykh)	133,36	16,74	47,37	695,82
11	3-sh5 brick light with brown intrusions	152,54	49,24	67,97	181,77
12	Brick (Masalli)	189,68	152,47	0	474,68
13	Vinofiline brick	1092,71	794,17	207,43	341,65
14	Industrial waste brick	1464.58	1066,93	278,38	420,63
15	Vinofiline brick	1555,00	1146,76	289,62	367,79
16	Industrial waste brick	2267.54	1651,85	430,13	666,04
17	Industrial waste brick	2390,83	1738,76	459,67	636,51
18	Industrial waste brick	3035.05	2200,56	578,3	980,99
19	Industrial waste brick	3808,99	2893,82	648,62	835,23

Table 3 presents data of gamma-spectrometric analysis of radioactive elements in different building materials.

According to the table C_{ef} of the tile varies greatly and depends on amount of natural radioactive elements therein. The paints are active due to potassium existing therein.

Table 3. C_{ef} and amount of radioactive elements in different building materials

№ №	Name	C_{ef}, Bq/kg	Amount of radioactive elements, Bq/kg		
			U (Ra)	Th	K
1	Window frame	0	0	0	0
2	White paint	4,66	0	0	59,51
3	White paint STR KO	9,92	0	0	126,62
4	Bulgarian tile	62,80	28,14	14,80	194,81
5	Greenish tile	171,25	70,82	62,15	242,37
6	“Slavyanski” tile	225,88	96,04	82,55	276,77

A special attention should be paid to concrete and cement and to goods made of them. There were cases when lost sources of radioactive radiation were occasionally buried in blocks. People and especially children who lived in flats constructed of such blocks were exposed to a strong irradiation with a lethal end. It is very important to know what cement and concrete are made of.

Once we revealed sources of ionizing radiation in cement on the floor in a shop in a students’ hostels. It turned out that the cement had been mixed on the base of iodine factory waste, namely on activized coal containing a high amount of radium. There was conducted disactivation and cleaning of the shop and now it has a normal radioactive background. Another object of radiation hazard are materials used for the isolation of the heating system. Such objects are asbestos pipes.

So we tried to present information about unfavorable radiometric monitoring of the building material. We would like to attract “Gosstroy’s” attention to the necessity to develop standards on amount of radionuclides in the building materials and to intensity radiometric monitoring in this field.

Solution of these problems is possible only on the base of analysis of results of wide-range gamma-spectrometric examination of the building materials.

Methodical documentation on this examination is available in “Radiometry” laboratory in ANAS.

RADIONUCLIDE CONTAMINATION OF NATURAL ENVIRONMENT OF ABSHERON PENINSULA (AZERBAIJAN)

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1. Introduction

The territory of Azerbaijan Republic is a unique object for ecological researches due to its geological, structure, geographical situation, combination of nature-climate zones and industrial potential.

One of the most ecologically problematic regions of Azerbaijan is Absheron Peninsula (total area 2,5ths.sq.km). Absheron peninsula is not only the high-populated area but also the same time main agricultural and oil-gas-producing region of Republic, where oil-gas fields exploration have been carried out for more than 150 years.

The main factors of pollution here are oil products from exploration fields.

2. Natural radioactive background

The territory of Absheron peninsula is composed by weakly-radioactive rocks, that is closely related to its geotectonic evolution.

Throughout the Absheron peninsula intensity of gamma-radiation varies from 3,5 to 7 μR/h. At the Shakhov spit and at the north coast beaches it decreases to 3 μR/h. On the other hand at the fields of mud breccia [4], at the areas of young travertine accumulations and within the areas of Maykopian rocks outcrops it increases to 9-30 μR/h.

Statistic parameters demonstrate normal radioactivity distribution with the average 6 μR/h (0,5 mSv/year), i.e. it is up to the level favorable to human residing. (Fig.1).

Correlation of these data with results of studies conducted in France, Germany, Italy, Japan and USA demonstrated that nearly 95% of population live in places where dose of radiation is 0,3-0,6 mSv/year as well.

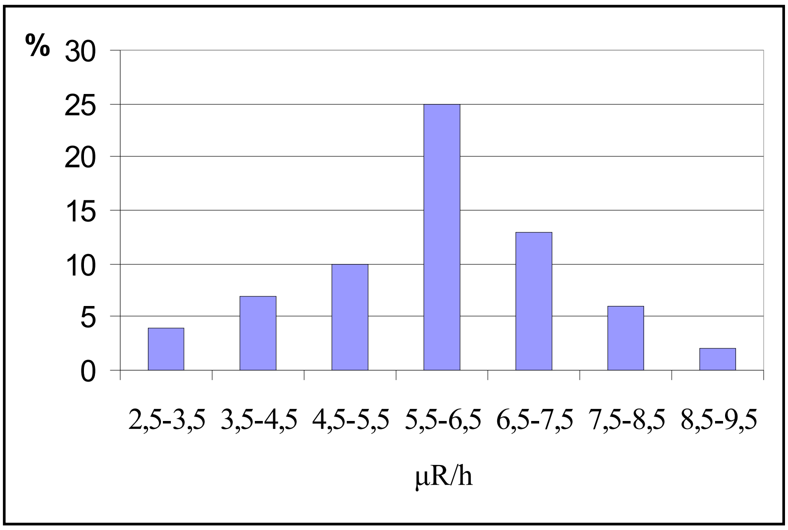

Fig. 1. Histogram of radioactivity distribution at the Absheron peninsula

3. Radionuclide contamination at the oil fields

The problem of oil-producing areas pollution by the natural origin radionuclides has arisen recently. Polluted by radionuclides surfaces and oil equipment are discovered at almost all exploration fields surrounding the capital and large industrial center of Azerbaijan - Baku city [1]. Anomalous areas where intensity of gamma-radiation reaches 600 μR/h (Fig. 2) were determined there.

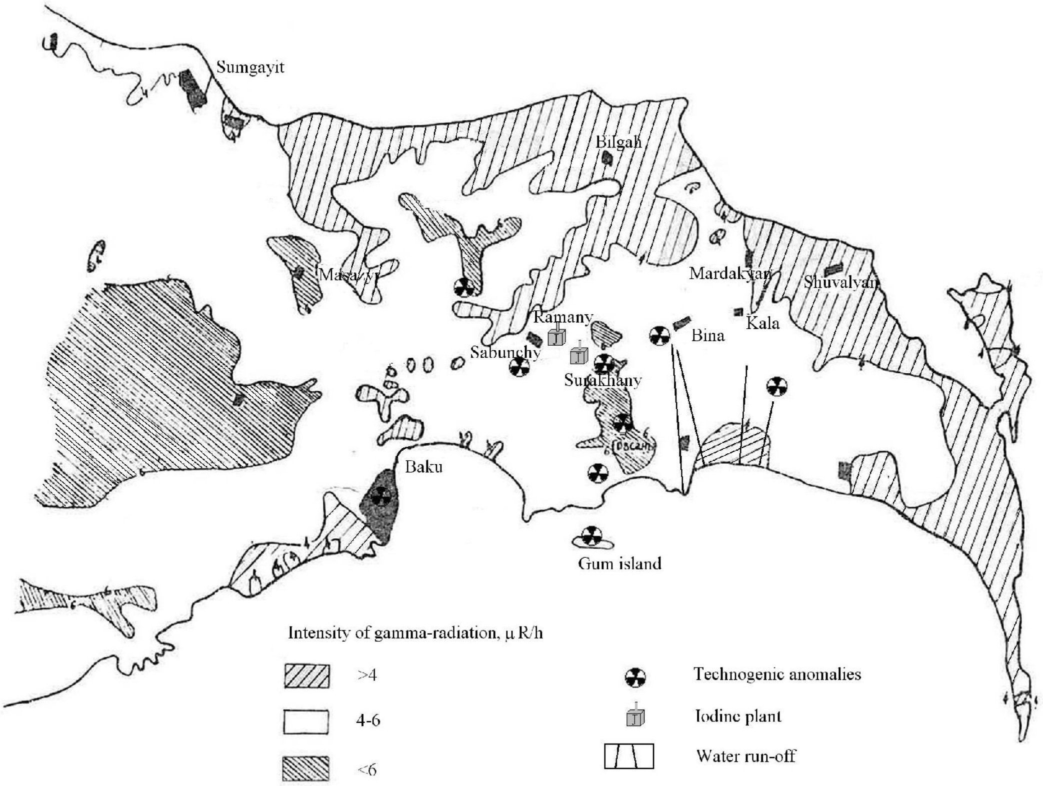

Fig. 2. Location scheme of zones with increased radioactivity at the Absheron peninsula.

Soils at several oil fields are heavily contaminated by radionuclides and sometime are probably subject to disposal as radioactive waste (!). It was determined that during the production, processing, transportation and preservation of oil and oil products there occurs intensive contamination of equipment, pipe-lines, reservoirs and surrounding environment.

A great amount of “contaminated” equipment (pipes, pumps, etc.) with a long-term radioactive background “crusts” (Fig. 3) is found out at the territory of oil fields. It represents high risk also because sometimes these equipment utilized or simply used by local inhabitants (for example, radioactive pipes serve as fences in kindergardens and school, etc.). Production made from such metal is very hazardous especially if it is used for construction of buildings [2].

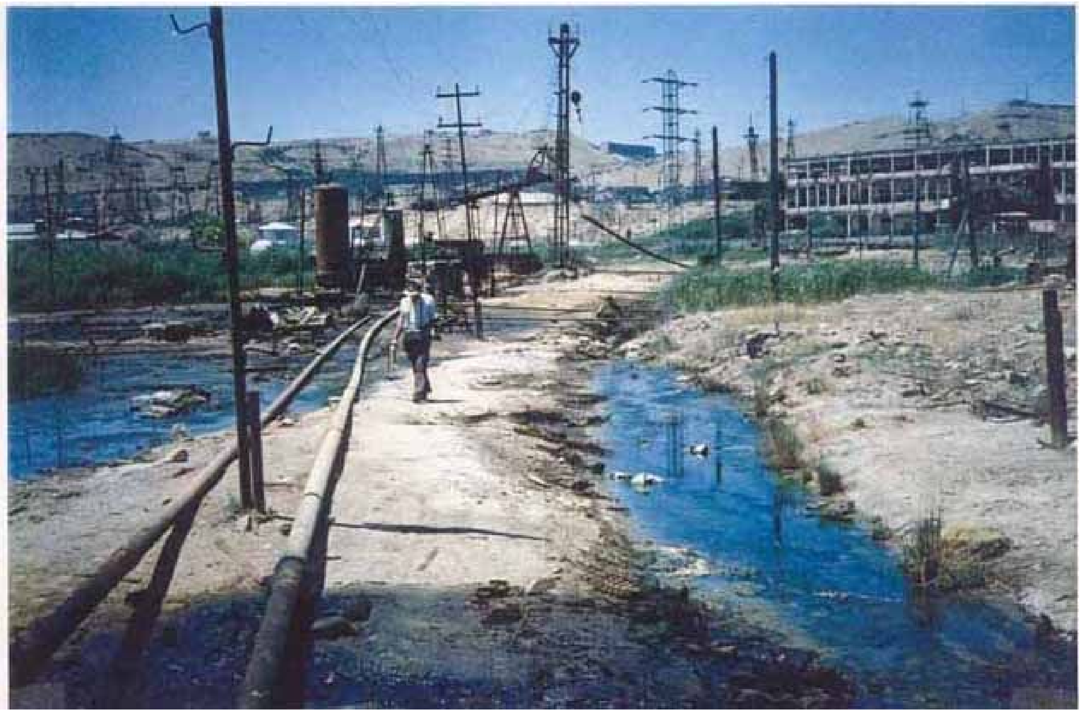

Fig. 3. Contamination of the oil field territory.

3.1 Radionuclides in waters from oil fields

Main contaminants at oil fields are radium and uranium depending on type of ground waters accompanying oil.

By their chemical composition stratal waters in the Absheron peninsula are divided into two main types [6,7]:

1. Hard chlorine-calcium-natrium,
2. Alkaline-hydrocarbonate-natrium.

Hard stratal waters at oil fields in contrast to other widely spread in the earth crust types of waters are carriers of the highest concentration of radium. The most common concentration of radium in such waters is $3\text{-}8 \cdot 10^{-11}$% that thousand times exceeds concentration ($2 \cdot 10^{-14}$%) in the oceanic water. With a rare exception concentration of radium in the waters of mineral springs is close only to the lower limit of amount of radium in oil waters. One can observe a dramatic deviation from average amount to both sites. The highest amount of radium is $2 \cdot 10^{-8}$%.

In oil waters concentration of some isotopes (mainly ^{228}Ra, ^{224}Ra) of a thorium series is also very high.

As a result of numerous investigations it was determined that high-mineralized hard sulphate-free waters of chlorine-calcium-natrium type containing high amount of alkaline earth elements are enriched by radium and its isotopes [5].

Petroleum waters became radium-bearing due to the leaching out of radium from rocks with a usual amount of radium. In the dispersed state radium always present in rocks. Radium seeps into stratal waters by means of capillary and fracture waters.

Radium is accumulated in sulphate-free chloride brines during the exchange desorbtion from clayey particles of rocks at a term of its presence in a layer of metamorphized waters of marine sedimentation.

Waters of the second type (alkaline waters) differ by a low amount of radium, but they are most favourable for concentration of uranium.

Uranium presents in all stratal waters in oil fields in the Absheron peninsula. Concentration of uranium in the alkaline waters does not drop below $n \cdot 10^{-6}$ g/l (for hard waters it is lesser than $n \cdot 10^{-7}$ g/l). Any rigorous regular relation between mineralization of hard waters and uranium amount has not been determined yet [3, 9].

Hard waters in comparison with oceanic waters are impoverished by uranium 5 times at an average. Enriching of alkaline waters by uranium depends on many factors including form of presence of uranium in waters and rocks and on character of its distribution in the system “oil- water”. Minimum and maximum numbers of uranium amount in the alkaline stratal waters in oil fields differ by 100 and more times (Table 1).

Table 1. Amount of radioelements in waters of main hydrochemical types at oil fields of Absheron p-la

Hydrochemical type of waters	**Amount of radioelements**		
	Uranium, g/l	Radium 10^{-11}, g/l	Thorium 10^{-7}, g/l
Alkaline	$5 \cdot 10^{-6}$	7,0	1,0
Hard	$4 \cdot 10^{-7}$	2,5	1,0

A typical feature of radioactive pollutions of the Absheron peninsula territory is that the pollution is made by radioactive isotopes of a natural origin but as a result of technogenic processes.

Dynamics of such oil fields pollution can be modeled rather simply.

Radioelements are evacuated to the earth surface by stratal and petroleum waters. Territories within and surrounding oil fields are contaminated most of all. Together with water and sand oil goes to a terminal by pipes. After initial separation oil is poured out and by pipes goes to oil refining plant. The water is discharged into artificial reservoirs where very radioactive loads are deposited and formed radioactive silty-muddy surface.

Contamination of new areas occurs rather quickly. Monitoring has shown, for example, that during the period of 5 years level of gamma-field changed from 4 mcR/h to 600-700 mcR/h at the absolutely clean territory of isle Gum (shallow marine area of the Caspian Sea) [3, 9].

Existence of a mobile contact of water with rocks and oil during its production plays a great role during the formation of contaminated areas in oil fields.

One of the methods of reducing the ecological intensity on the oil fields can be the refining and utilization of subsurface waters and underground salt brines with the following, probably, their usage for the medical goals.

4. Radionuclide contamination in the territories of iodine pants

Besides, within the Absheron peninsula there are two iodine plants, the territory of which is also polluted by radionuclides of the natural origin.

Extraction of iodine and bromine from the stratal waters is associated with the accumulation of radium in the activated coal. With the coarse of time the coal is accumulated in the territories of plants (Fig. 4).

Wind and precipitation spread radionuclides around the plants and contaminate the nearest populated areas. Level of gamma-radiation within such territories sometimes reaches 1000 μR/hour (with background of 6 μR/hour). In the areas polluted by iodine plants (beyond the territories) amount of radium at the earth surface exceeds the background 1000-2000 times [8].

The identification of the radionuclides showed that the group of uranium-radium (the content of which reaches the high concentrations) is presented here.

Fig. 4. Environmental contamination by iodine plants. On the left – accumulations of high-radioactive activated coal.

Conclusion

Different mechanisms of anomalies formation depend on numerous geological and hydrogeological factors. Results of investigation demonstrate that mitigation of contamination or its liquidation is a difficult task and fist of all it is necessary to examine hydrogeochemical environment at different territories.

During the exploration of oil fields it is necessary to take environmental protection measures even before geologic-exploration works especially it is almost obligatory to make researches linked with the study of radiation background

High potential for the solution of the above-mentioned problems exists and different leading oil companies (like “bp”) understand it as well. Radiation safety should be provided by concrete measures of control for its state and by the observation and implementation of requirements of “The Low of Radiation Safety” adopted in 1997.

References

1. Aliyev Ch.S., Podoprigorenko M.V., Zolotovitskaya T.A., 1996. Radionuclide pollution of environment during oil fields exploration. ANH, №7, Baku, p. 46-50. (in Russian)
2. Aliyev Ch.S., Djahanguiri F., Reimer M., Zolotovitskaya T.A 1997. Radioactive contamination of oil fields of Apsheron peninsula. SPE/EPA. Dallas, Texas, USA.
3. Aliyev F.G., Aliyev Ch.S., Aliyeva E.A., Zotovitskaya T.A., 1999. Processes of formation of radionuclide contamination in oil fields. Proceedings of the 5th Baku International Conference. “Energy, Ecology, Economy”, Baku, p.516-519.
4. Aliyev Ch.S., Feyzullayev A.A., Zolotovitskaya T.A., Aliyeva S.K. et al., 2001. Radioactive fields of mud volcanoes of Azerbaijan. Geophysics news in Azerbaijan. №3, p.25-32.

5. Efendiyev G.H., Alekperov R.A. Nuriyev A.N., 1964. Questions of radioactive elements geochemistry of oil fields. Published by Academy of Sciences of Azerbaijan SSR, Baku, 150 p. (in Russian)
6. Geology of Azerbaijan/ hydrogeology/ ed. O.K. Lange – Baku: Academy of Sciences of Azerbaijan SSR. 1961, p.136-183. (in Russian)
7. Geology of USSR/Azerbaijan SSR, geological description/ ed. Sh.A. Azizbekov, M: Nedra, 1972, v.47, 620 p. (in Russian)
8. Zolotovitskaya T.A., Aliyev Ch.S., 1995. Absheron peninsula, radioecological conditions. Proceedings of the Second Baku International symposium: “Energy, Ecology, Economy”. Baku, printed in Tabriz University, JRG, Iran, Baku p.70-77.
9. Zolotovitskaya T.A., 2003. Mechanisms of formation of radionuclide contamination at the oil fields of Azerbaijan. N.Birsen and K.K. Kadyrzhanov (eds.), Environmental protection against Radioactive Pollution. Kluwer Academic Publishers. Netherlands, p.75-77

MITIGATION METHODS IN SELECTION PLACES OF CONSTRUCTION SITES

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One of the primary tasks in selection of construction sites is study of the geological structure. Tectonic faults within construction sites represent additional serious hazard for buildings. Application of radiometric methods allows us to determine activity of fault dislocations. In radioactive fields of the earth crust only active tectonic dislocations and geodynamic zones manifest themselves.

While planning construction works it is necessary to locate buildings outside the hazardous areas. Results of surveys allowed us to identify areas with increased radon exhalation. According to level of gamma-radiation areas of grounds of different lithologic composition are identified. It mitigates risk of hazardous radiation for people.

Tectonic disturbances regardless of what they are: through or “blind” (buried) faults play role of hydrodynamic drainage systems. Constant microfluctuations accompanying tectonic activity form favourable environment for rising fluid streams. Researches showed that cracks in the upper beds could be formed not only in the zone of through faults, but over zones of buried active structures. The latter are more dangerous for constructions, i.e. overlapped fault becomes the source for additional microfluctuations and fluid transportation. These faults can't be observed in engineering research, but they can show their influence on radioactive fields regardless of thickness of overlapping series (Fig.1).

There is a great similarity between radioactive and wave fields. So, many gamma-lineaments stretch along zones of complex seismic information, that is identified with zones of high tensity of media surrounding fault-line area. They are large tectonic elements in both fields – like Baku trough surrounded by a ring of anticlinal folds. These folds are represented by gradients of seismic waves rates in wave field, in radioactive – by change of intensity of gamma-radiation on isoline 5 μR/h. Especially Fatmai-Zykh folded zone can clearly be observed both in seismic and in radioactive field. Borders of active faults zones are clearly recognized by radiometric methods in particular by gamma-survey. It's important to define the area of dynamic influence of a fault especially when the fault doesn't goes up to surface. By combined study of radioactive and seismic wave fields it has been established that difraction area is confined to fault zone in the upper part of sedimentary series. They show a high extent of microjointing and a high fluid-permeability for migration of radioelements to surface. That is how anomalies of gamma-field are formed over the zones of active-tectonic dislocations. In this case the problem of danger of one or another tectonic dislocation can be solved by radiometric methods.

For instance, the dislocations which aren't reflected in gamma-field serve as a screen for seismic waves (here their attenuation occurred) and this decreases amplitude, i.e. seismic danger is reduced (Fig. 2).

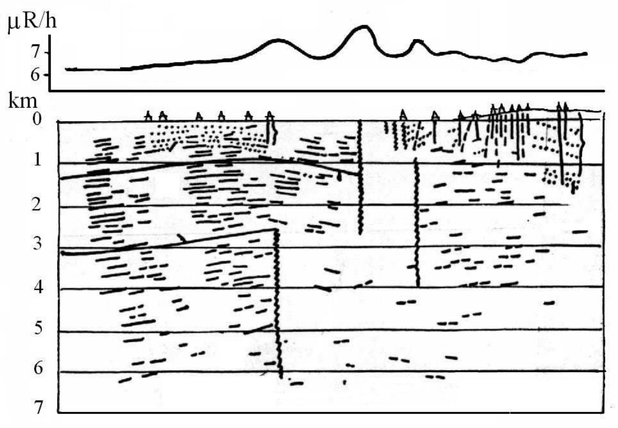

Fig. 1 Actively living tectonic disturbances manifesting in radioactive field regardless of thickness of overlapping series.

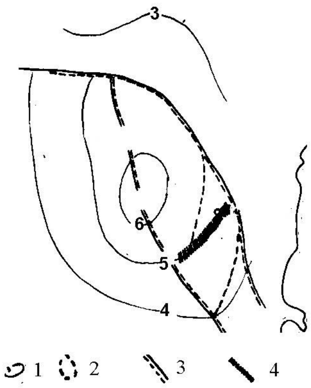

Fig. 2 Misrepresentation of macroseismic field of Kura earthquake dealing with screening activity of consolidated tectonic disturbances.

1 – isoseismal line; 2 – theoretic isoseismal line; 3,4 – tectonic fault.

Non-traditional complexity of radiometric methods with seismic survey, electrometry, gravimetry and space data allowed to distinguish heterogeneity in earth crust on intensity of their manifestation in radioactive fields.

It has been established that geodynamically active parts of the Earth crust are reflected by contrast anomalies both in radioactive fields and on the space photos.

At the same time a number of dislocations revealed in other geophysical fields (e.g. in gravity field) manifested neither in gamma-field nor on space photos.

Considering this the classification of zones of tectonic dislocations is presented on intensity of their manifestations in radioactive fields and on the space photos.

1. Faults completed their development are weakly manifested in radioactive field although they find their reflection in other geophysical fields. These heterogeneities of earth crust don't reflect on space photos.
2. Faults inherited and continuing their development are manifested in radioactive field by positive contrast gamma-lineaments, regardless of thickness of sediment bulk overlapped the zone of dislocations as under influence of constant vibration in the layer overlapping the "blind" fault the zone of high fluid permeability is formed.
3. Faults formed on the modern stage of development are presented by a poor-radioactive anomalies. The degree of their activity is determined on isotope relation values of Ra^{228} and Ra^{226}. In accordance with it the intensity of manifestations of geodynamical processes is estimated. They are usually reflected on the cosmic photos, but are poorly manifested in other geophysical fields.

Such a non-traditional complexity of the geophysical methods with the usage of remote sensing methods and macro-seismic data allowed us to contour and prove the existence of the heterogeneity zone in the earth crust of the South-Caspian depression of the anticaucasian direction, named by us the Eastern-Mugan zone of dislocations.

Below we will give some examples of the successive use of radiometric methods during the selection of construction sites with a minimum risk of earthquake. For the first time we used radiometrical methods for micro-seismic zonation on the construction site of the radio-broadcasting station (in Baku city).

As a result of it the zones of high tectonic activity, reflecting in gamma-field by high values of capacity of the expositional doze were determined and the place for tower construction situated on the non-geodynamic active zone was recommended as well, thus predetermined its safety (Fig. 3).

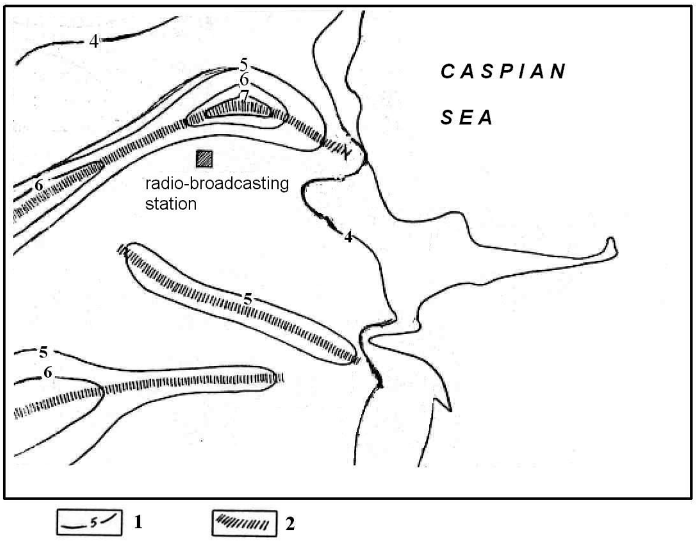

Fig. 3 The location of construction area of industrial complex relatively the zones of tectonic disturbances.

1 – isogamms; 2 – tectonic fault.

The spatial position of the North-Adjinour zone of tectonic dislocations of the caucasian direction and zone of the Kutkashen-Chykhyrly fault which direction is transverse to the structure of Caucasus was clarified by means of gamma-field. Thus, the best options for construction area due to the active zones were chosen (Fig. 4).

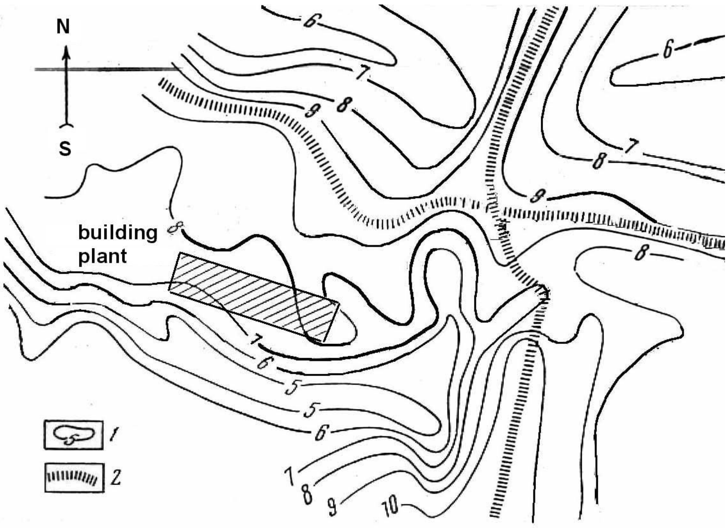

Fig. 4 The location of construction area of industrial complex relatively the zones of tectonic disturbances.

1 – isogamms; 2 – tectonic fault.

Results of carried out works become the basis for radiometric method application for the final selection of a building site for atomic electric station. During the designing process several competitive sites were chosen, four from which were recommended for further detail seismo-tectonic investigation (Fig. 5). For the revealing of spatial position of these sites and tectonic faults zones the auto-gamma survey on the territory with the area 800 sq.km was carried out. Studied territory represented mostly by the quaternary formations- proluvial-alluvial rocks that are homogenous by its composition. Within this lithologically homogenous field the radioactivity varied in a rather wide ranges - from 4 to 11 μR/h, reflecting the geological structure. On the transformed map the lineaments with a high values of radioactivity showing the relation of radioactivity of the given rock type to the normal background were determined. Its comparison with geological and tectonical maps, lineaments location (determined according to the cosmic photos) showed, that the Adjichai-Alyat fault zone found its reflection in the gamma-field. Thus, zones of tectonic dislocations were revealed and recommendations on the best sites location were given as well.

As a result of the conducted research 2 sites were defected, and for the rest the detailed radiometric works, allowing to estimate the seimic hazard, were conducted (Fig. 6).

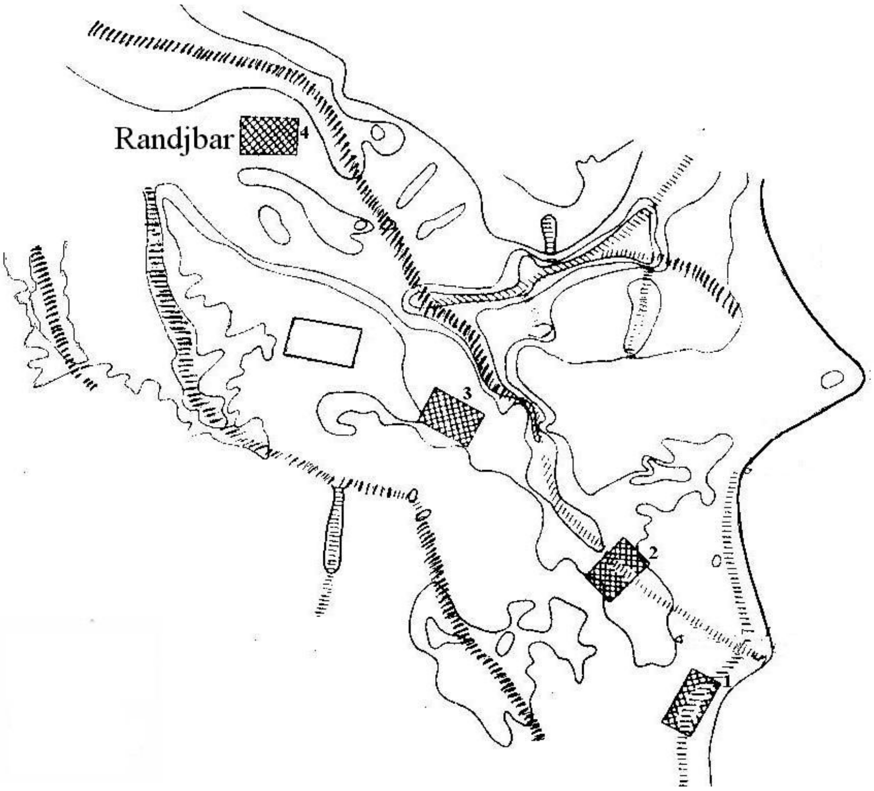

Fig. 5 The use of radiometry in study of competitive AES area on Azerbaijan territory.

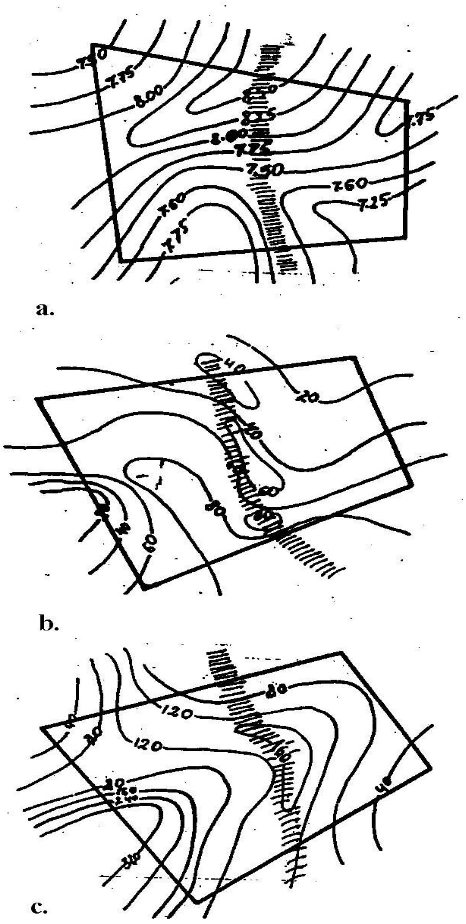

Fig. 6 Radioactive fields in “Salyanskaya-2” field.

a.– integral gamma-field; b. – by radon; c. – by thoron.

So, the radiometrical methods are successfully used in Azerbaijan for selection the most favourable zones for construction in the areas with a seismic risk and are considered to be an important link of research on decreasing the risk of earthquakes, radioactive ionization, especially on the stage of designing of important state constructions.

ENVIRONMENTAL RADIOLOGICAL IMPACT OF A DICALCIUM PHOSPHATE COMPLEX IN THE EBRO RIVER (SPAIN)

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Abstract

In this work we report the distribution of U and Th series radionuclides in the disposal area located in the vicinity of an industrial complex on the Ebro River shore. This industry produces dicalcium phosphate (DCP) used as a source of phosphorus and calcium for feeding domestic animals. The waste products of the industrial process are released into 5 dumping areas in the Flix hydroelectrical reservoir producing 5 sedimentary lobules near the river shore. A sediment core was collected from each lobule. The concentrations of natural radionuclides clearly showed the enhancement of concentrations in the sediments since the beginning of production in 1973. The observed activities ranged from 42-11000 Bq kg^{-1} (^{238}U), 32-5600 Bq kg^{-1} (^{210}Pb), 21-9900 Bq kg^{-1} (^{226}Ra) and 10-163 Bq kg^{-1} (^{232}Th). The total amount of radioactive material accumulated was estimated to be 130 - 240 GBq for ^{210}Pb, 220 - 420 GBq for ^{226}Ra, and 380-730 GBq for ^{238}U. These concentrations may be of concern as it is well known that radionuclides such as ^{210}Pb, ^{210}Po and ^{226}Ra can be accumulated by certain aquatic organisms.

Introduction

TE – NORM (Technological Enhancement of Natural Occurring Radioactivity) wastes are generated in numerous countries, as a result of the extraction and processing of natural resources such as oil and natural gas (scales and sludges in the production), coal or metals (e.g. zircon sand used in ceramic industry) and minerals (e.g. phosphorite used in phosphate industry) (Baxter, 1996; Baetsle, 1991; Rutherfords *et al.*, 1997). TE – NORM wastes release to the environment radionuclides associated with the U-238 and Th-232 natural decay chains in radioactive equilibrium. Therefore, it can cause such as radiation exposures to the population via direct exposure or via the food chain (Mc Donald *et al.,* 1996; Keating *et al.* 1996). For instance, the chemistry of ^{226}Ra is similar to that of calcium, and concentrates in the skeleton of the animals (Hakam *et al.*, 2001; UNSCEAR, 1993).

Dicalcium phosphate (DCP), phosphate fertilizers, and phosphoric acid are manufactured from phosphate rocks of sedimentary origin, which is known to contain elevated natural ^{238}U and its daughter products (1500-1700 Bq kg^{-1}) and a minor contribution of ^{232}Th (Azouazi, 2001; UNSCEAR, 1993). The by-products and waste materials of this industry (e.g phosphogypsum) represent an important input of radionuclides and trace metals into the natural ecosystems (Vandenhove, 2002; Keating *et al.* 1996).

The Flix factory (Tarragona) is composed by a plant of chlorine and caustic soda (since 1897) combined with a bicalcium phosphate plant (since 1973) located in the margin of the Flix reservoir in the Ebro River (Fig 2). The DCP production from Morocco's phosphate rock was initiated in 1973. Since then, the factory has produced DCP using the HCl from its chlorine plant, with an initial production of 70.000 Tm y^{-1} and a 30% increase during the nineties. At present time, DCP's production is 110.000 Tm y^{-1}. The residual formed sludge consists of $CaCl_2$, CaF_2 and undissolved phosphorite rock (SiO_2) rich in heavy metals.

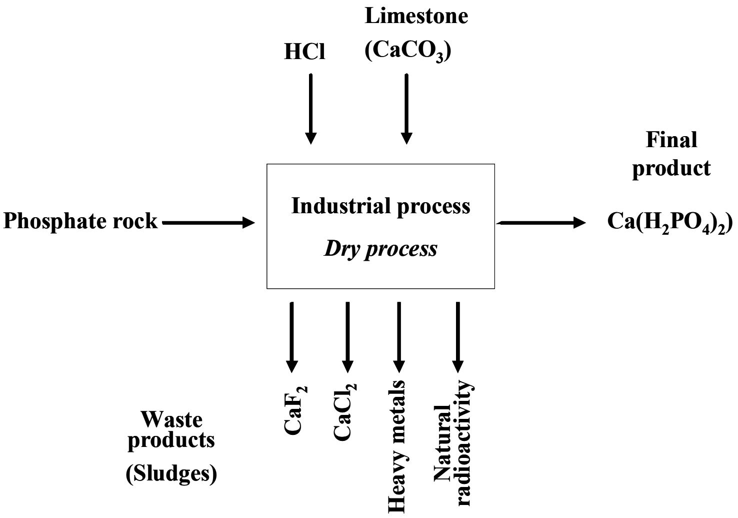


Fig. 1. Schematic illustration of the inputs and outputs of the industrial process

The natural radioactivity contained in the phosphorite used in the industrial process is distributed between final products and subproducts. The specific activity of Morocco's phosphorite was determined by Carvalho (1995), with average values of about 1000 Bq kg^{-1} for ^{238}U, ^{234}U and ^{210}Pb and 1400 Bq kg^{-1} for ^{226}Ra. Roessler *et al.,* (1978) state that the distribution of the natural radioactivity in the phosphate products, by-products and waste material depends on the technology used in the manufacturing process. Gäfvert *et al.* (2001) establish that 80% of ^{226}Ra was retained in the waste products. Additionally, the main ^{238}U concentrations were found in the DCP product. In contrast, the ^{210}Pb and ^{210}Po concentrations were equally distributed between the final product (DCP) and the waste material ($CaCl_2$) (Carvalho, 1995; Gäfvert *et al.* 2001).

The objective of the present study was to investigate the radioactivity levels in the waste materials of the DCP manufacturing plant dumped in the water reservoir.

Materials and Methods

Study area

The Flix reservoir was built in 1948 and is about 12 km long, with an average depth of 5 m. It covers an area of about 3.2 km^2 with a total capacity of 11.4 hm^3 and useful capacity of 4.5 hm^3. The reservoir dam is 15.50 m high and 400 m wide. The Ebro River has an average discharge flow of 13400 hm^3 y^{-1} (Ibañez, *et al.* 1999). From unpublished data, the total quantity of waste material disposed under the water ranges from 200 to 360·10^3 Tm.

Analyses

Five cores were collected from the dumping deltas in January 2001 by using a vibrocore. The lengths of the cores ranged from 77 cm to 250 cm and were sliced in 5 cm sections (Fig. 2). All samples were transferred into closed plastic bags and kept frozen until analysis.

Lead-210 measurements were performed by alpha-spectrometry by using silicon surface barrier detectors connected to a multichannel analyser. Approximately 0,150 g of dried and powdered sediment sample of each section were spiked with ^{209}Po as a yield tracer. After total dissolution of the sample the activities were determined after spontaneous deposition of the polonium onto a silver disc assuming secular equilibrium with ^{210}Po (Sanchez-Cabeza *et al.* 1998). Uranium and thorium activities in the sediments were determined by using a low-background HPGe gamma well-detector (*Canberra*). The detector was calibrated using standard samples with a radionuclide activity certified by IAEA, and contrasted using an self laboratory efficiency simulation program supported in MCNP code. Furthermore, the accuracy of measurements is confirmed by participation in intercomparison exercises between

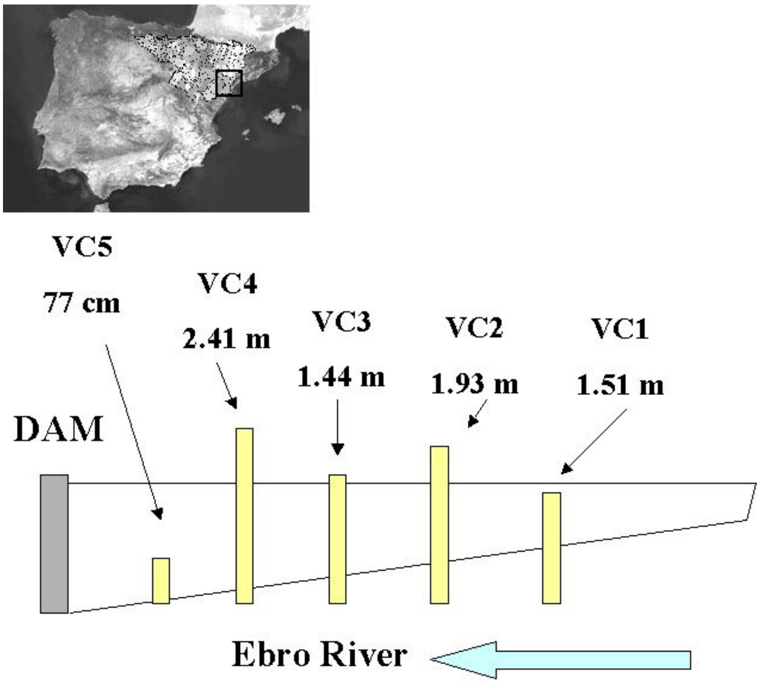


Fig. 2. Core samples collected in the Flix reservoir (Ebro river), close to the chlor-alkali and bicalcium phosphate factory (DCP).

different laboratories. Approximately 5 g of dry powdered sample was placed into a plastic geometry. After a 21-day in-growth period, samples were measured for ^{226}Ra, ^{238}U, ^{232}Th, and ^{40}K. ^{226}Ra activities were determined through the activity of ^{214}Pb at 351.9 keV, in secular equilibrium with ^{226}Ra. Activity concentrations of ^{238}U were determined from the emission lines of ^{234}Th, and ^{232}Th activities via gamma emission lines of ^{228}Ac.

Results and discussion

The average and maximum activity values of ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K for the five cores are given in Tables 1 and 2, respectively. The activity profiles of each core are displayed in Figure 3.

From these results it is apparent that there is an enhancement in the activities of uranium and thorium series in the waste material located in the vicinity of the Flix chlor-alkali and bicalcium phosphate plant since 1973, when DCP production was initiated. The most notable results were obtained for deeper sediments in the core VC5 and for upper sediments in the core VC3, with highest activities of 3500 Bq·kg^{-1} for ^{210}Pb (VC5), 9361 Bq·kg^{-1} for ^{226}Ra and 11723 Bq·kg^{-1} for ^{238}U (VC3), about 500 times higher than the background values of the river sediments. VC1 core is the only one in which ^{137}Cs is detected. It is well known that ^{137}Cs can be used to establish chronological marks in sediments when post-depositional processes are not affecting the distribution of this radionuclide (Sanchez-Cabeza *et al.,* 1999). ^{137}Cs has an artificial origin from the nuclear atmospheric tests since 1954, with a peak of concentration in the atmosphere in 1963, and another peak in Europe caused by the Chernobyl accident in 1986. Therefore, according to the ^{137}Cs activity profile we could assume that the whole core was deposited after 1954. Additionally, and based on the beginning of DCP production when the factory releases started (1973), the layers of sediment core affected by anthropogenic inputs of Te-norm waste materials can be distinguished of the paleolacustric riverbed sediments at 99-102 cm depth.

Our results are similar to other local enhancements due to phosphatic discharges described in the literature (Table 3). For instance, in the northern basin of the Venice Lagoon, Guogang *et al.* (2003) reported an average value of ^{210}Pb of 6700 Bq kg^{-1} in phosphogypsum collected at the disposal site close to a industrial Tenorm zone, which is about 260 times higher than the lagoon background levels. In the salt marshes of the Odiel and Tinto estuary (southwest of Spain) Martinez-Aguirre & Garcia-León (1997) found values that ranged from 15.4±10.1 to 820±27 Bq kg^{-1} for ^{210}Pb, and 20.3±17.7 to 711±45 Bq kg^{-1} for ^{226}Ra in soils of the marsh. McCarteney *et al.* (2000) found concentrations of ^{238}U, ^{210}Pb, and ^{210}Po of 685±17, 140±2, 7750±200 Bq kg^{-1}, respectively, in the sediments of Whitehaven harbour (Cumbria coast) due to phosphoric acid plant discharges. Papastefanou (2001) estimated the emissions from a phosphate processing plant located in Thessaloniki (Northern Greece) in 10 MBq of ^{238}U and ^{226}Ra per year. Carvalho

(1995) estimated the input of dissolved ^{210}Pb through the discharge of the Tagus River in 21 GBq y^{-1} due to the influence of phosphate ore processing industry.

Radiological impact

Based on a study carried out previously in the Flix reservoir, the total amount of waste material disposed under the water of the Flix reservoir is estimated in 200 to $360 \cdot 10^3$ Tm. (A. Palanques, unpublished data). Thus, the total amount of radioactive material present was estimated to be 130 - 240 GBq for ^{210}Pb, 220 - 420 GBq for ^{226}Ra, and 380-730 GBq for ^{238}U. In Spain, the NORM wastes are governed by the European directive *CEC, 1996, Council Directive 96/29/Euratom* with the values of the Table 4. The UE-directive essentially mirrors the International Atomic Energy Agency Basic Safety Standards for Protection against Ionizing Radiations and for the Safety of Radiation Sources (BSS) (IAEA Safety series No. 115, 1996). (Seitz, R.R., 2000).

Consequently, the Flix wastes in some samples are just slightly below the exemption concentration levels for ^{210}Pb and ^{226}Ra. But in some instances ^{238}U activity concentrations are above these limits. In addition, the total radioactive inventory is above the exempted.

Table 1. Range activity concentrations of selected radionuclides of 5 sediment cores collected in the waste material deltas in the Flix reservoir.

Core code	**Contaminated zone**			**Non contaminated zone**		
	^{210}Pb	**^{226}Ra**	**^{238}U**	**^{210}Pb**	**^{226}Ra**	**^{238}U**
VC1[*]	140±6 to 410±11	280±5 to 900±43	590±28 to 1700±52	30±2 to 57±3	24±5 to 42±9	37±9
VC2	83±5 to 800±37	133±7 to 990±21	590±24 to 1900±35	3.2±0.8 to 57±3	21±5 to 56±5	42±10 to 130±10
VC3	170±6 to 1350±49	110±20 to 9361±181	1883±29 to 11723±198	6.3±0.7 to 39±2		105±14

VC4	97±3 to 540±24	140±7 to 1280±22	140±14 to 680±28	5.4±0.7 to 25±2	24±10 to 76±16	49±16 to 110±3
VC5	820±24 to 3500±157	300±10 to 1620±315	170±14 to 3530±322			

*VC1 = 5±2 to 8±3 Bq kg^{-1} (^{137}Cs)

Radionuclide	**VC1 (Bq kg^{-1})**	**VC2 (Bq kg^{-1})**	**VC3 (Bq kg^{-1})**	**VC4 (Bq kg^{-1})**	**VC5 (Bq kg^{-1})**
^{40}K	816 ± 51	- -	283 ± 55	135 ± 38	462 ± 36
^{226}Ra	900 ± 34	959 ± 20	9361 ± 181	1283 ± 22	2052 ± 26
^{137}Cs	8 ± 3				
^{232}Th	48 ± 8	61 ± 9	219 ± 13	70 ± 7	69 ± 6
^{238}U	1684 ± 25	1902 ± 25	11723± 198	682 ± 28	3533 ± 223
^{210}Pb	412 ± 11	802 ± 37	1353 ± 49	535 ± 24	3545 ± 157

Table 2. Maximum activity concentrations of ^{40}K, ^{226}Ra, ^{137}Cs, ^{232}Th, ^{238}U measured in the core samples.

Table 3. Activity values of some Tenorm material

Location	**Environment**	**Tenorm material**	**Reference**	**Average activity (Bq kg^{-1})**		
				^{210}Pb	**^{226}Ra**	**^{238}U**
Florida (USA)	Stockpiles-stored		Hull & Burnett (1996)		1600	1500
Portugal	Tajo estuary	Phosphogypsum	Carvalho, J., (1995)		1043	156
Sweden	Stockpiles-stored	Phosphoric rock (Morocco)	Carvalho, J., (1995)	1083	1406	1003
		Dicalcium phosphate	Gäfvert et al. (2001)	169	15	954
		Waste material of bicalcium phosphate production	Gäfvert et al. (2001)	100	142	8.0
	Stockpiles-stored	$CaCl_2$	Gäfvert, et al. (2001)	3480	78	
Italy	Venice lagooon (1)	Phosphogypsum	Guogang et al. (2003)	6725		

Morocco	Phosphate mines	Phosphogypsum	Azouazi et al., (2001)		1420	<1700
	Sediments of the eastern Irish sea	Phosphate ore mix	Poole et al., (1995)	837	1477	1377
Spain	Tinto & Odiel estuary	Soil-marshland	Martinez-Aguirre & Garcia León (1997)	15.4 to 820	20.3 to 711	
Spain	Odiel river	River sediments	Periañez et al. (1997)	341		
Spain	Ebro river	Waste material of bicalcium phosphate production	This work	1526	1841	6158

Table 4. Exemption TE-Norm levels of the Council Directive 96/29/Euratom

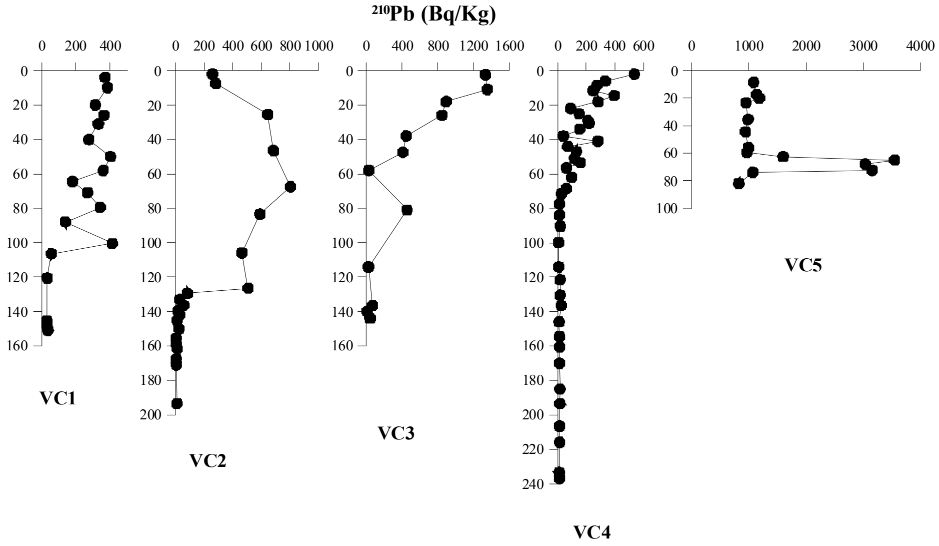
Nuclide	**Exemption TE – NORM levels** (96/29/Euratom)	
	Quantity (Bq)	**Concentration (Bq kg^{-1})**
^{226}Ra^{+}	10^4	10.000
^{210}Pb^{+}	10^4	10.000
^{210}Po	10^4	1.000
^{232}Th	10^3	1.000
^{238}U	10^3	1.000

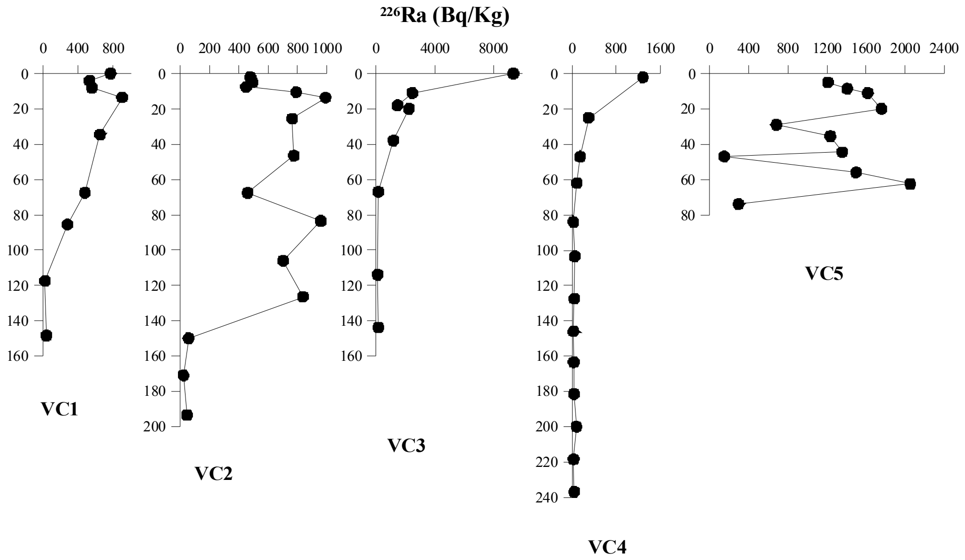
values of total quantity of activity. Thus, these Tenorm materials should be considered as waste material radioactive and be declared. For instance, during the dismantling process of nuclear reactors, it is common practice to declassify wastes with levels ranging from 100 to 200 Bq·kg^{-1} for ^{238}U and other radioactive emitters. Assuming that, Flix TENORM waste materials should be considered radioactive waste.

Conclusions

An important Tenorm enhancement has been detected in the sediments of the Flix reservoir, due to phosphate discharges from the Flix-DCP plant. The highest activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th in the sediments of Flix reservoir were 11723±198, 9361±181, 3545±157, and 219±13 Bq kg^{-1}, respectively. The average activity concentrations are about 308 (^{238}U), 92 (^{226}Ra) and 38 (^{210}Pb) times higher than the background levels in natural sediments of the river.

The global radioactive inventory displays values above the total quantity of radiation allowed by the Council directive, CEC (1996). Thus, these Tenorm materials should be considered as radioactive and be declared as such.


^{210}Pb (Bq/Kg)
0 200 400
0 200 400 600 800 1000
0 400 800 1200 1600
0 200 400 600
0 1000 2000 3000 4000
0 20 40 60 80 100 120 140 160
0 20 40 60 80 100 120 140 160 180 200
0 20 40 60 80 100 120 140 160
0 20 40 60 80 100 120 140 160 180 200 220 240
0 20 40 60 80 100
VC1
VC2
VC3
VC4
VC5


^{226}Ra (Bq/Kg)
0 400 800
0 200 400 600 800 1000
0 4000 8000
0 800 1600
0 400 800 1200 1600 2000 2400
0 20 40 60 80 100 120 140 160
0 20 40 60 80 100 120 140 160 180 200
0 20 40 60 80 100 120 140 160
0 20 40 60 80 100 120 140 160 180 200 220 240
0 20 40 60 80
VC1
VC2
VC3
VC4
VC5

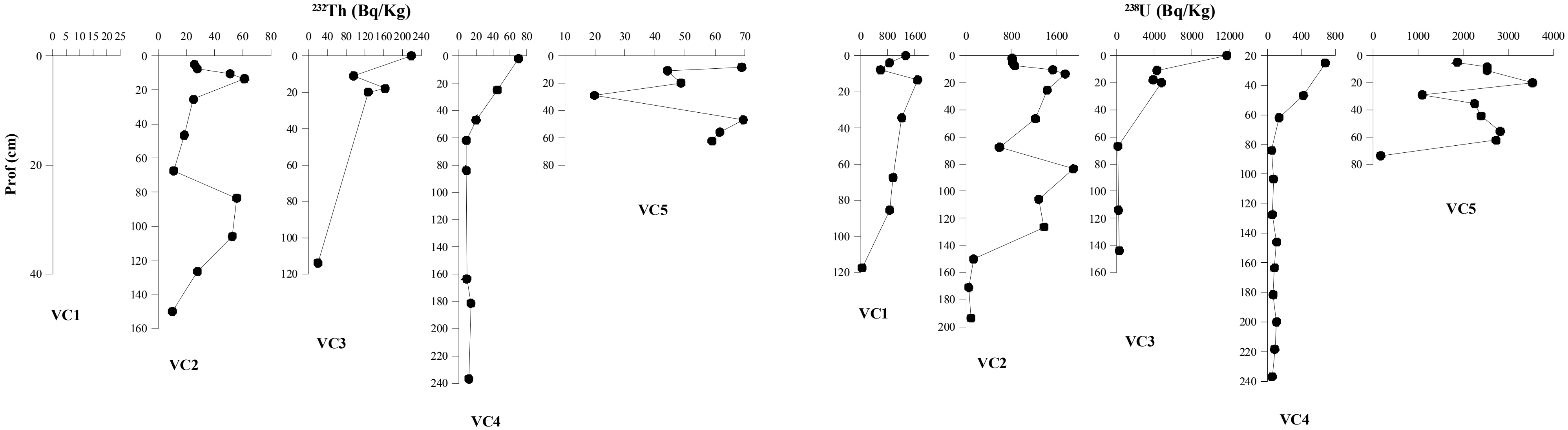


Fig. 3. Vertical profiles of activity concentrations of ^{210}Pb, ^{226}Ra, ^{232}Th, ^{238}U (Bq kg^{-1} dry wt.) in 5 sediment cores collected from the dumping waste material lobules in the vicinity of the Flix factory.

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References

Azouazi, M., Ouahidi, Y., Fakhi, S., Andres, Y., Abbe, J.Ch., Benmansour, M., (2001). Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco. *Journal of Environmental Radioactivity* **54**, 231-242.

Baetslé, L.H. (1991). Study of the radioanuclides contained in wastes produced by the phosphate industry and their environment. Comission of the European Communities, EUR 13262 EN, Nuclear Science and Technology.

Baxter, M.S., (1996). Technologically Enhanced Radioactivity An Overview. *J. Environ. Radioactivity.* **32**, **1-2**, 3-17.

Carvalho, J., (1995). 210Pb and 210Po in sediments and suspended matter in the Tagus estuary, Portugal. Local enhancement of natural levels by wastes from phosphate ore processing industry. The *Science of the Total Environment* **159**, 201-214.

CEC, (1996). Council Directive 96/29/Euratom of 13 May 1996 laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionising radiation. Official Journal of the European Communities, L 159/1, June 29, p. 45.

Gäfvert, T., Holm, E., Roos, P. (2001). Radionuclide fluxes at a plant manufacturing dicalcium phosphate for domestic animals. Journal of Environmental Radioactivity, **54**, (1), 61-73.

Guogang Jia, M. Belli, U. Sansone, S. Rosamilia, M. Blasi, (2003). ^{210}Pb and ^{210}Po concentrations in the Venice lagoon ecosystem (Italy) and the potential radiological impact to the local public and environment*. Journal of Radioanalytical and Nuclear Chemistry*, **256** (3), 513-528.

Hull, C.D. & Burnett W.C. (1996). Radiochemistry of Florida Phosphogypsum. *Journal of Environmental Radioactivity* **32**, 213-238.

Ibañez, C.; Prat, N; Canicio, A. i Curcó, A. (1999). El delta del Ebro, un sistema amenazado. Bakeaz, Coagret. Zaragoza. p. 109.

Hakam, O.K., Choukri, A., Reyss, J.L., Lferde, M., (2001). Determination and comparison of uranium and radium isotopes activities and activity ratios in samples from some natural water sources in Morocco. *J. Environ. Radioact.* **57**, 175-189.

IAEA Safety series No. 115 (1996). International basic safety standards for protection against ionizing radiation and for the safety of radiation sources, Vienna.

Keating, Gillian E., McCartney, M., Davidson, Christine M., (1996). Investigation of the Technological enhancement of Natural Decay series Radionuclides by the manufacture of phosphates on Cumbria coast. *J. Environ. Radioactivity,* **32**, 53-66.

Martínez-Aguirre, A. & García-León, M., (1997). Radioactive impact of phosphate ore processing in a wet marshland in southwestern spain. *Journal of Environmental Radioactivity* **34**, 45-57.

McCartney, M., Davidson, C.M., Howe, S.E., Keating, G.E., (2000). Temporal changes in the distribution of natural radionuclides along the Cumbrian coast following the reduction of discharges from a phophoric acid production plant. Journal of Environmental Radioactivity, **49**, 279-291.

McDonald, P., Baxter M.S., Scott, E.M. (1996). Technological enhancement of natural radionuclides in the marine environment. *Journal of Environmental Radioactivity* **32**, 67-90.

Papastefanou, C., (2001). Radiological impact from atmospheric releases of ^{238}U and ^{226}Ra from phosphate rock processing plants. *Journal of Environmental Radioactivity* **54**, 75-83.

Periáñez, R. & Martínez-Aguirre, A. (1997). Uranium and thorium concentration in an estuary affected by phosphate fertilizer processiong: experimental results and a modelling study. *Journal of Environmental Radioactivity* **35**, 281-304.

Poole, A.J., Allington, D.J., and Denoon, D.C., (1995). Temporal and spatial survey of dissolved ^{226}Ra in coastal waters of the eastern Irish Sea. *Science of The Total Environment* , **168** (3), 233-247.

Roessler, C.E., Smith, Z.A., Bolch, W.E. & Prince, R.J. (1978). Uranium and Radium-226 in Florida phophate material. Heatlh Phys., **37**, 269-77.

Rutherford, P.M., Dudas, M.J., Samek, R.A. (1994); Environmental Impacts of Phosphogypsum; Sci Total Environ, **149**, 1-38.

Sanchez-Cabeza, J.A., Masqué, P. i Ani-Ragolta, I. (1998). Pb-210 and Po-210 analysis in sediments and soils by microwave acid digestion. *Journal of Radioanalytical and Nuclear Chemistry* **227**, 19-22.

Sanchez-Cabeza, J.A., Masqué, P.,Martínez-Alonso M., Mir J. & Esteve I. (1999). ^{210}Pb Atmospheric flux and growth rates of a microbial mat from the northwestern Mediterranean sea (Ebro river Delta). *Environmental Science & Technology* **33,** 3711-3715.

Seitz R., (2000). Disposal of waste containing technologically enhanced concentrations of naturally occurring radioactive materials-when is it a concern?. WM 2000 Conference, Tucson.

UNSCEAR (1993). Sources and Effects of Ionising Radiation, UNSCEAR Report to the General Assembly, United Nations, New York 1993, p. 18.

Vandenhove, H., (2002). European sites contaminated by residues from the ore-extracting and -processing industries. *International Congress Series* **1225**, 307–315

EVALUATION OF OCCUPATIONAL RADIOLOGICAL EXPOSURES ASSOCIATED WITH FLY ASHES FROM FRENCH COAL POWER PLANTS

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Abstract

The French Ministry of Health is preparing a series of decrees for transposing into French regulation the Euratom 96/29 Directive title VII concerning in particular the work activities where natural radioactive substances are handled and used, but not for their radioactive, fertile or fissile properties. Coal power stations belong to a list of industrial sectors potentially concerned by this transposition and the decrees' calendar of preparation includes a consultation period allowing to collect information about the possible dosimetric impacts on various population groups of these industrial sectors. At the request of the two French operators of coal power stations, Electricité de France (EDF) and the National Company of Electricity and Thermics (SNET), CEPN has evaluated occupational radiological exposures resulting from the industrial activities which bring into play fly ashes produced by the French coal power stations. In a first step, the various stages of the French fly ashes cycle were studied, namely their production, handling and transport, storage, and recycling (mainly in building materials and road works). In a second step, reference groups of workers likely to receive significant doses were identified. Finally, a series of exposure scenarios, aiming to be both conservative and realistic, were described on the basis of realistic exposure data (when available) together with generic values and simplifying assumptions. In the absence of dosimetric measurements, individual exposures were evaluated using appropriate models for external irradiation, dust and radon inhalation, ingestion and transfer in the biosphere. Estimated annual individual doses range from fractions to hundreds of microsieverts per year and maximum doses are associated with situations (tailings works, road construction) where external contribution is slightly dominating. Sensitivity analyses were performed to evaluate the impact on dose estimates of possible variations of the calculation parameters. This study should provide both industrial and regulatory bodies with a methodological approach enabling to pinpoint situations in the French context that may be calling for a particular attention in terms of radiation protection. This paper summarises the assessment methodology as well as the characteristics and associated individual doses of the most important scenarios.

1. Introduction

The French Ministry for Health is currently preparing a series of decrees for transposing in French regulation the Euratom 96/29 Directive, particularly the title VII relating to work activities where natural radioactive substances are handled and used, not for their radioactive, fertile or fissile properties [1, 2, 3]. The calendar of preparation of these decrees has envisaged a consultation period in order to collect information about the dosimetric impacts of such activities on various population groups (workers and members of the public). In this context, Electricité de France (EDF) and the National Company of Electricity and Thermics (LA SNET), the two French operators of coal power stations, have asked CEPN to evaluate occupational and public radiological exposures resulting from the French industrial activities which bring into play fly ashes produced by coal power stations. In this paper, only occupational exposure situations are presented [4].

In a first step, the various stages of the French fly ashes cycle (from their production to their storage or final use) were studied, namely their handling and transport, storage, physicochemical transformations, and recycling (mainly in building materials and road constructions). For each stage, the sources, exposure places and physical / chemical properties of fly ashes and their by-products were described. In a second step, different reference groups of workers likely to receive significant doses were identified. A series of exposure scenarios, aiming to be both conservative and realistic, were defined on the basis of actual data (when available) together with generic parameter values and simplifying assumptions.

Complementarily, sensitivity analyses were performed in order to identify the main calculation parameters, *i.e.* those which variation would impact the most the dose estimates.

2. Data used for the assessment

2.1. French fly ashes cycle

The combustion of coal in French power stations produces each year an estimated volume of about 2 million tons of fly ashes that varies according to the energy demand. At present, the totality of the produced fly ashes is recycled, and tips are even regularly retrieved. As shown on Table I, coal fly ashes are largely used in building materials and road works. They can be sent from the power station immediately after being produced, but the seasonality of road works (especially in winter) may require fly ashes to be temporarily stored. In that case, fly ashes are humidified and then deposited in basins (short transit storage) or on tips, and further retrieved according to the demand.

Table I. Production and use of fly ashes in France – 1996-2000 averages [5].

	$kt.y^{-1}$	%
Use		
Concrete + prefabricated material	749	42
Cements	425	24
Road works	392	22
Embankments	157	9
Other	79	3
Total	**1802**	**100**
Production	**1930**	

2.2. Physical and chemical properties of fly ashes

The physical and chemical properties of fly ashes depend upon the composition of the coal and the combustion process by which fly ashes are formed. In France, power stations currently use in a large majority coal imported from South Africa – the use of lignite in the single remaining power station of Gardanne is to be stopped soon –, in “classical” fluidised wet-bottom boilers. The chemical composition of fly ashes is of the silicate-aluminate type, with low calcium oxide content.

2.3. Radionuclides content of fly ashes

The radioactivity of fly ashes mainly comes from potassium-40, and from the uranium-238 and thorium-232 decay chains (maximum values respectively found to be 1700, 250 and 200 $Bq.kg^{-1}$). The radionuclides content of fly ashes varies according to the origin of coal. For the present study, 20 fly ashes samples coming from French power stations were considered. Taking account of the various measurement limitations, the activity concentrations of radionuclides that were either not measured or below detection limit, as well as values measured with a relative uncertainty greater than 50%, were replaced by values derived from a secular equilibrium hypothesis. Three types of typical fly ashes were artificially derived from these 20 samples, which will be referred in the following as: "low-level" where radionuclide contents were all set to the lowest measured values, "high-level" where radionuclide contents were all set to the highest measured values and "mean-level". Results show that, for each radionuclide, maximum activity concentration values are roughly fourfold higher than minimum values (see Table II).

Table II. Radionuclide contents of fly ashes considered in the study.

Radionuclide	Low-level Bq.kg^{-1}	High-level Bq.kg^{-1}	Mean-level Bq.kg^{-1}	Standard deviation
U-238	**54**	**246**	**133,9**	**59,1**
Th-234	54	246	133,9	59,1
Pa-234m	54	360	160,3	90,8
Pa-234	0,2	1,2	0,5	0,3
U-234	54	246	133,9	59,1
Th-230	38	246	118,3	60
Ra-226	44	260	138	75,6
Po-218	44	260	138	75,6
At-218	44	260	138	75,6
Pb-214	47	231	117,5	58,8
Bi-214	45	231	112,2	57
Po-214	47	231	117,5	58,8
Pb-210	29	274	116,8	64,8
Bi-210	29	274	116,8	64,8
Po-210	29	274	116,8	64,8
Th-232	**66**	**173**	**119,3**	**39,2**
Ra-228	66	173	119,3	39,2
Ac-228	66	173	119,3	39,2
Th-228	66	190	123,6	42,4
Ra-224	66	190	123,6	42,4
Po-216	66	190	123,6	42,4
Pb-212	65	180	128,2	39,7
Bi-212	73	200	133,5	42,6
Po-212	42	122	79,2	27,2
Tl-208	23	62,3	44,7	14,4
K-40	**170**	**1703**	**955,6**	**481,7**

3. Methodology and assumptions

3.1. Methodology

The methodology consisted in:

a) the identification of exposure situations within thermal coal power stations and within the major fly ashes-recycling industries in building materials and road works sectors,

b) the elaboration, for these situations, of exposure scenarios for reference groups of persons,

c) the calculation of individual exposures associated with those scenarios.

In the absence of direct dosimetric measurements, individual exposures were evaluated using models requiring, for each scenario, particular information mainly relating to:

- sources: physical form, geometry, air dust concentration, release rate from power station stack, radionuclide contents of stack emissions, effective release height, meteorological conditions…
- exposure places: location/distance to the radioactive source, time spent at this place, existence of possible radiological protections (natural or artificial protective shields against external irradiation, respiratory protections against inhalation)…
- physicochemical properties of fly ashes and by-products: specific activity, chemical composition, particle size distribution, density, porosity, permeability…

In this paper, only occupational exposure situations are presented.

3.2. Exposure situations

Workplaces potentially leading to a significant radiological exposure due to the vicinity of fly ashes were identified: five of them are associated with the thermal coal power stations and four are associated with the fly ashes transport/recycling industries. The pertinence of these situations has been confirmed during a visit in a French coal power station.

In coal power stations, the exposure situations considered are the following:

1. Boiler ash box, used for the retrieving of bottom ashes, filled with water, in front of which a person is supposed to work periodically to remove ashes from it.
2. Plant silos, storage silos for dry fly ashes beside which an ashes handling agent is supposed to spend time during fly ashes trucks loading or during fly ashes humidification before loading.
3. Hoppers under electrostatic precipitators, beside which a person is supposed to spend time when rounding for surveillance, or during repair or maintenance operations.
4. Electrostatic precipitators, inside which a person is supposed to spend time for repair or maintenance operations.
5. Tip works, involving a person in a vehicle on the fly ashes tip for continuous ash-levelling or trucks loading.

In the transport/recycling industry, the exposure situations considered are the following:

1. Truck, beside which a person is supposed to spend time during loading/downloading operations and transportation of dry or wet fly ashes from power plants to fly ashes-recycling industries.
2. Concrete factory, where a person is supposed to be exposed to fly ashes storage silos and to loaded concrete trucks during his duties.
4. Road works, where a person is supposed to be exposed to fly ashes used as embankments or as aggregates in road sub-layers.

5. Building materials factory, where a person is supposed to work close to a pile of building materials containing fly ashes as a partial substitute for cement.

For each situation, external irradiation was taken into account. Ambient dose rates associated with the radionuclides contained in fly ashes were calculated using the Microshield [6] software, considering adequate protective shields where necessary. Where relevant, inhalation of airborne dust was evaluated considering -in absence of more precise information- an air dust load of 10 mg.m-3, this conservative value corresponding to the French occupational regulatory limit of airborne dust concentration without compulsory wearing of respiratory protective equipment [7]. Radon inhalation was also considered where relevant.

3.3. Annual exposure scenarios

The exposure situations identified above were combined with annual work durations associated with different jobs, in order to elaborate realistic exposure scenarios. Conservative assumptions of annual work duration were made where this information could not be obtained precisely, in particular for repetitive tasks for which several operators could be involved over a whole year, rather than a single one.

Table III. Description of exposure scenarios.

Exposure situation	Scenario	Exposure duration for one operation	Annual duration for a single person
1. Boiler ash box	Emptying of the boiler ashes box	2 h per emptying, every 24 h	Maximum 178 operations over a year, *i.e.* 356 $h.y^{-1}$
3. Hoppers under electrostatic precipitators	Round in the room under electrostatic precipitators	10 min per round; 2 rounds per 8-hour period	Maximum 178 rounds over a year, *i.e.* 60 $h.y^{-1}$
3. Hoppers under electrostatic precipitators	Maintenance in the room under electrostatic precipitators	80 h over a year	40 $h.y^{-1}$ for a single person
4. Electrostatic precipitators	Maintenance inside electrostatic precipitators		88 $h.y^{-1}$ for a single person
2. Plant silos	Loading/downloading trucks	1/2 h per operation, twice a day	For truck driver, 2 h per day, 200 d per year, *i.e.* 400 $h.y^{-1}$

6. Truck	Transport of fly ashes	3 h per round (half of it with empty truck)	For truck driver, twice a day, 200 d per year, *i.e.* 600 h.y^{-1}
2. Plant silos	Humidification of fly ashes	1/2 h per truck, 4 trucks per day	40 d per year, *i.e.* 80 h.y^{-1}
5. Tip works	Ash-moving on tips	8 h per day	200 d per year, *i.e.* 1600 h.y^{-1}
7. Concrete factory	Concrete factory	8 h per day	200 d per year, *i.e.* 1600 h.y^{-1}
8. Road works	Road works	8 h per day	200 d per year, *i.e.* 1600 h.y^{-1}
9. Building materials	Building materials factory	8 h per day	200 d per year, *i.e.* 1600 h.y^{-1}

4. Results

4.1. Individual doses

For all scenarios abovementioned, the annual individual doses calculated for the “mean-level” fly ashes radioactivity content are less or equal to 500 μSv.y^{-1}.

The highest individual doses are associated with works in the vicinity of large volumes of fly ashes, with a major contribution of external irradiation:

- Tips works: 500 μSv.y^{-1} (60% from external irradiation);
- Road works: 310 μSv.y^{-1} (54% from external irradiation).

4.2. Exposure routes and radionuclides contribution

In situations where the person is exposed to a large volume of fly ashes, external irradiation predominates over the other sources of exposure (it represents about 60% of the total exposure in roads and tips works). In other situations involving relatively smaller volumes of fly ashes, airborne dust inhalation becomes a predominant exposure route, keeping in mind that the air dust load (10 mg.m^{-3}) is a crucial parameter in this evaluation.

The radionuclides associated with the ^{232}Th decay chain mainly contribute to the external exposure (segments [^{228}Ra, ^{228}Ac] and [^{228}Th to ^{208}Tl] represent approximately half of the total external exposure). The segment [^{226}Ra to ^{214}Po] of the ^{238}U decay chain represents about 30% of the external exposure, and ^{40}K represents 23% of it.

Similarly, radionuclides associated with the ^{232}Th decay chain mainly contribute to the exposure from airborne dust inhalation (^{228}Th, ^{232}Th and ^{224}Ra represent about 60% of the total exposure from airborne dust inhalation). ^{40}K does not contribute significantly to this exposure route.

Radon inhalation contributes significantly to the total exposure (maximum 25% of total) only when the person is exposed indoors (as compared with open air situations). It is the case for the employee of a building materials factory.

4.3. Sensitivity analysis of the results

The exposure scenarios presented in this study were elaborated on the basis of hypotheses that seemed realistic in the French context, but were nevertheless designed to be conservative. To provide quantitative elements to better evaluate the situation in a wide range of possible contexts, a sensitivity analysis of the results to the various calculation parameters was performed. A synthesis of this analysis is presented in Table IV at the end of this paper. The following paragraphs present the application of the major sensitivity analysis results to the two exposure scenarios associated with the highest individual doses estimated in this study, *i.e.* the ash-moving on tips and the road works.

One of the critical parameters used is the radionuclides content of fly ashes, which may vary. However, even if one considers the “high-level” radioactivity fly ashes content derived from the 20 samples considered in this study, the maximum annual individual dose would remain below the French regulatory limit of 1000 μSv.y^{-1} for non-exposed workers.

As far as tip works are concerned, keeping in mind the respective contributions of the major exposure routes – 54% from external irradiation for a 0.3 cm cabin steel thickness and 45% from air dust inhalation –, the sensitivity of calculated doses to the exposure parameters is as follows:

- Increasing the steel thickness of the cabin from 0.3 to 0.6 cm would reduce the exposure from external irradiation by a factor of about 1.4;
- The distance to the source has no significant effect;
- The size of the tip has no significant effect as soon as its surface is greater than an equivalent 20 m radius disk and its depth is greater than 0.4 m;
- The contribution of radon to the exposure may be neglected;
- The dose associated with dust inhalation is directly proportional to the considered airborne dust concentration.

As far as road works are concerned, keeping in mind the respective contributions of the major exposure routes – 64% from external irradiation and 40% from airborne dust inhalation for an ash content of 10% in mass in road aggregates and an airborne dust load of 10 mg.m^{-3} –, the sensitivity of calculated doses to the exposure parameters is as follows:

- The size of the embankment or road aggregate sub-layer has no significant effect as soon as the surface is greater than an equivalent 5 m radius disk and the depth is greater than 0.4 m,
- The contribution of radon to the exposure can be neglected,
- Exposures from external irradiation and airborne dust inhalation are directly proportional to the fly ashes content of aggregates,
- The dose associated with dust inhalation is directly proportional to the considered airborne dust concentration.

5. Conclusion

This study allowed to estimate the radiological exposures associated with fly ashes produced by thermal coal power stations in France. The considered occupational exposure scenarios tackled various exposure situations: five of them dealt with the activities within thermal coal power stations (jobs situated near significant volumes of fly ashes, directly connected to the fly ashes moving, transport and stocking operations). Four specific additional scenarios were studied in the fly ashes-recycling industries (building and road works).

For each situation, the following exposure routes were considered (when relevant): external irradiation, inhalation of airborne dust and radon. These predominant exposure routes were selected on the basis of data extracted from the literature and from the preliminary estimates performed within the framework of this study with EDF and LA SNET.

The annual individual doses estimated for the various persons concerned by the scenarios considered in this study are less than the French regulatory dose limit for non-exposed workers (1 mSv.y^{-1}). The highest value (0.5 mSv.y^{-1}) - associated with fly ashes which “mean-level” radioactivity content was derived from the analysis of 20 fly ashes samples supplied by EDF and LA SNET - concerns ash-moving tip works.

It must be noted that the estimated doses rely on parameters that influence the results in a direct way, such as:

- The annual exposure duration and the level of radioactivity of fly ashes: the annual total dose is directly proportional to these parameters; as regards the annual exposure duration, it was voluntarily very conservatively estimated in this study,
- The airborne dust concentration: the exposure by inhalation is directly proportional to this parameter. In absence of more realistic data, the value

considered in this study is the French regulatory limit of 10 mg.m^{-3}, which seems to be a very conservative estimate. In this context, the inhalation represents 45% of the total annual dose for the employee on fly ashes tips.

It could be envisaged to perform complementary measurements of the radioactivity in fly ashes according to the place of production and to the origin of coals in order to get a better assessment of the French situation and to conduct *in situ* measurements of ambient dose rates and airborne dust concentration to validate the major assumptions made in this study.

6. References

1. Directive 96-29/EURATOM du 13 mai 1996 fixant les normes de base relatives à la protection sanitaire de la population et des travailleurs contre les dangers résultant des rayonnements ionisants (1996).
2. Décret 2003-296 du 31 mars 2003 relatif à la protection des travailleurs contre les dangers des rayonnements ionisants (2003).
3. Décret 2002-460 du 04 avril 2002 relatif à la protection générale des personnes contre les dangers des rayonnements ionisants (2002).
4. Lepicard S., Degrange J-P., *Evaluation des expositions radiologiques associées aux cendres volantes produites par les centrales thermiques à charbon en France: exposition des travailleurs*, CEPN NTE/03/04 (2003).
5. EDF - LA SNET, Personal Communication (2003).
6. MICROSHIELD, Version 5, Grove Engineering (1996).
7. Cahier de notes documentaires – hygiène et sécurité du travail, *Valeurs limites d'exposition aux agents chimiques en France*, N°174, 1er trimestre (1999).

Table IV Detailed results from sensitivity analysis

Parameter	Value considered	Sensitivity
ALL EXPOSURE ROUTES		
Fly ashes activity concentration		Annual dose directly proportional (according to the relative contribution of each radionuclide)
Exposure duration		Annual dose directly proportional
EXTERNAL IRRADIATION		
Thickness of steel		Quasi linear: at 1 m from the source, dose rate is divided by 1.4 if the thickness of steel is doubled. This effect is less pronounced if the distance to the source increases
Silo	1 cm	
Cabin of tip ash-moving machine	0.3 cm	
Height of fly ashes		
Tip	10 m	Beyond a 1 m height, no influence on the dose rate; less than 1% difference between 1 m and 0.4 m
Silo (axial)	15 m	
Aggregates in road sub-layers	0.4 m	
Road embankments	6 m	
Distance to the source		
Axial (under a 5 m radius silo)	5 m	Dose rate multiplied by 2.4 when going from 5 m to 1 m; division by 3 from 5 m to 10 m
Axial (under a 1 m radius hopper, 2 m from the axis)	2 m	Dose rate multiplied by 1.5 going from 2 m to 1 m
Radial (beside a 5 m radius silo)	1 m from the silo (6 m from the axis)	Dose rate divided by 2.3 when going from 1 m to 5 m and divided by 3.8 from 5 m to 25 m
Radial (beside a 1 m radius and 2 m height hopper)	1 m from the hopper	Dose rate divided by 1.5 when going from 1 m to 2 m; divided by 4.6 from 1 m to 5 m
Distance to tip surface	1 m	Less than 3% difference when going from 1 m to 3 m
Tip surface	10^5 m^2	No effect as soon as the surface is greater than 10^3 m^2 (equivalent to a 20 m radius disk)
Fly ashes content of the material		
Road aggregates and building materials	10% (in mass)	Dose rate directly proportional to the fly ashes content
DUST INHALATION		
Air dust load	10 mg.m^{-3}	Dose rate directly proportional to the air dust load
Fly ashes content of the material		
Road aggregates and building materials	10% (in mass)	Dose rate directly proportional to the fly ashes content
RADON INHALATION		
Effective diffusion coefficient	5.10^{-7} m^2.s^{-1}	Exhalation rate multiplied by 1.3 when doubling the diffusion coefficient; division by 2.3 when dividing by 5 the diffusion coefficient
Tip surface	10^5 m^2	Outdoor radon air concentration multiplied by 3 when multiplying by 10 the surface; division by 10 when dividing by 100 the surface
Source density	1	The exhalation rate is directly proportional to the source density
Source depth		
Tip	10 m	Beyond 4 m, no effect on the exhalation rate, even for the highest diffusion coefficient

Room/source volumes ratio Pile of building materials	4	Indoor radon concentration conversely proportional to the room/source volumes ratio

RECYCLING OF Th-232 CONTAMINATED TUNGSTEN SCRAP

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Introduction / Abstract:

In Krefeld, Germany, Siempelkamp operates a melting plant to treat metal scrap contaminated with natural radioactivity, mercury and other chemical and toxical substances. The so-called GERTA plant is licensed according to the German BImSchG (federal law on protection against environmental pollution).

The facility is equipped with a mains frequency induction furnace and has an annual licensed capacity of 2,000 t. The purpose is to decontaminate metal scrap for recycling in the steel cycle without any limitations.

So far the input has been carbon or stainless steel with contamination of Ra-226 as main nuclide in case of NORM contamination, or mercury from oil and gas producing facilities or from chlorine electrolysis.

In a recent project, over 130 t of tungsten and molybdenum alloyed with thorium oxide from the welding electrodes and filaments production have been successfully decontaminated and converted into a Fe-W-Mo alloy, which could be marketed as a high value product. By this way, up to 25 wt-% of tungsten/molybdenum could be solved in an iron melt and the thorium-oxide could be transferred to the slag.

The slag could be released by the 1 mSv/a-criteria for workers and population in accordance with the German radiation protection ordinance.

In an expert opinion it was found out that according to the typical distribution of throughput in the GERTA plant specific activities up to 65 Bq/g Th-232 and 87 Bq/g Ra-226 can be accepted, when 100 t/year of slag are recycled to road construction material.

This paper describes the “tungsten project” in terms of metallurgy, radiation protection and legislation.

Siempelkamp´s Melting Facilities

Since 1883, the Siempelkamp group operates a foundry with a current capacity of more than 60,000 t of ductile cast iron per year at their main site in Krefeld, Germany. In the beginning of the 1980´s, the Siempelkamp foundry developed a process to melt low radioactively contaminated scrap originating from maintenance and decommissioning projects of nuclear power plants. The so-called CARLA facility (central facility to recycle low radioactive materials) is licensed according to the German Radiation Protection Ordinance since 1989 and is still unique in Germany. Treating metals is limited up to a specific activity of 200 Bq/g with the exemption of 2,000 Bq/g for low beta emitters (H-3, C-14, Fe-55 and Ni-63) and 1,000 Bq/g for scrap contaminated by naturally occurred radioactive materials (NORM). The value for the contamination with fissible radionuclides is limited at 15 g/100 kg scrap in accordance with the German atomic law.

The aim of melting radioactive scrap is to minimize the volume of scrap to be disposed of as radioactive waste, to decontaminate the metal and to homogenize remaining radionuclides in the melt. Depending on the remaining activity, the options for reuse of the produced CARLA ingots are:

- ingots below release limits can be used as input for conventional recycling paths,
- ingots above these limits are reused for manufacturing casks or shieldings for application in the nuclear cycle.

In case ingots should not be qualified for recycling, they will have to be stored for decay before release or for final disposal, when an atomic depository will be in operation.

In 1998, the GERTA facility (large scale melting plant for recycling hazardous wastes) started operation at the site in Krefeld. Siempelkamp has developed this recycling process in 1996 as a spin-off from the CARLA process especially to treat scrap cross contaminated with NORM and mercury.

The GERTA plant is licensed according to the German BImSchG (federal law on protection against environmental pollution) and can process chemically-/ toxically contaminated scrap (e.g. mercury, asbestos, PCB, furanes, dioxines) as well as NORM contamination up to 500 Bq/g. The final metal product is completely free of all contamination and can be released to the steel cycle without any limitations [1].

Use of Tungsten-Molybdenum-Thorium Alloys

The use of tungsten and its alloys spreads over a wide variety of applications due to its properties like high density (19,25 g/cm³), a melting point of 3,410 °C and a hardness from 4,5 – 8 (Moh´s scale).

Examples for the different basic and final products are

- Ferro – Tungsten (70 – 85 wt.-% W) as an additive for alloyed steel

- Tungsten – Powder (99,99 %) as an additive for non ferrous alloys
- Tungsten – Carbides (W$_2$C, WC)
- Filaments, welding rods (Tungsten – Molybdenum – Thorium - Alloys):

Figure 1 shows examples of production residues of W-Fe-Th materials.

Figure 1: Filament and pressed powder residues

Filaments and welding rods are made of a W-Fe-Th alloy. Up to 4 wt.-% of radioactive ThO$_2$ and a certain amount of molybdenum are sintered with tungsten powder to enhance the properties of tungsten for the use in filaments and welding rods **[2].** This leads to activity levels of up to 65 Bq/g Th-232sec for the particular alloy. The average activity of the residues, which have been processed at Siempelkamp in the current project was 12 Bq/g.

According to that fact, the treatment of the thorium contaminated material as well as the production residues for instance grinding sludge, filament fragments, pressed powder etc., needs special monitoring according to appendix XI, § 96 respectively § 102 of the German Radiation Protection Ordinance. Recycling of tungsten thorium alloys is not allowed according to current legislation, if no prior decontamination took place, whereas the tungsten ferrous- and non-ferrous - alloys and carbides can be handled as conventional material for recycling.

Chemical and Radiological Aspects of the Melting Process

After 5 years of experience with steel scrap contaminated with products of the uranium – and radium decay chain, Siempelkamp invented a process to decontaminate tungsten – thorium alloys and to transform the tungsten into a reusable product. It takes place in a net frequency induction furnace with a capacity of 8 Mg per batch. The melting process has to be started with a 3 Mg sump of liquid iron followed by a batch of 5 Mg of scrap. The furnace can be operated in the temperature range from 1,350 °C up to 1,500 °C. The average melting time is 4 hours which leads to a capacity of 30 Mg per day. Additives like silica-carbides and carbon amount to 4 wt-% of the input. Figure 2 shows schematically the GERTA melting plant.

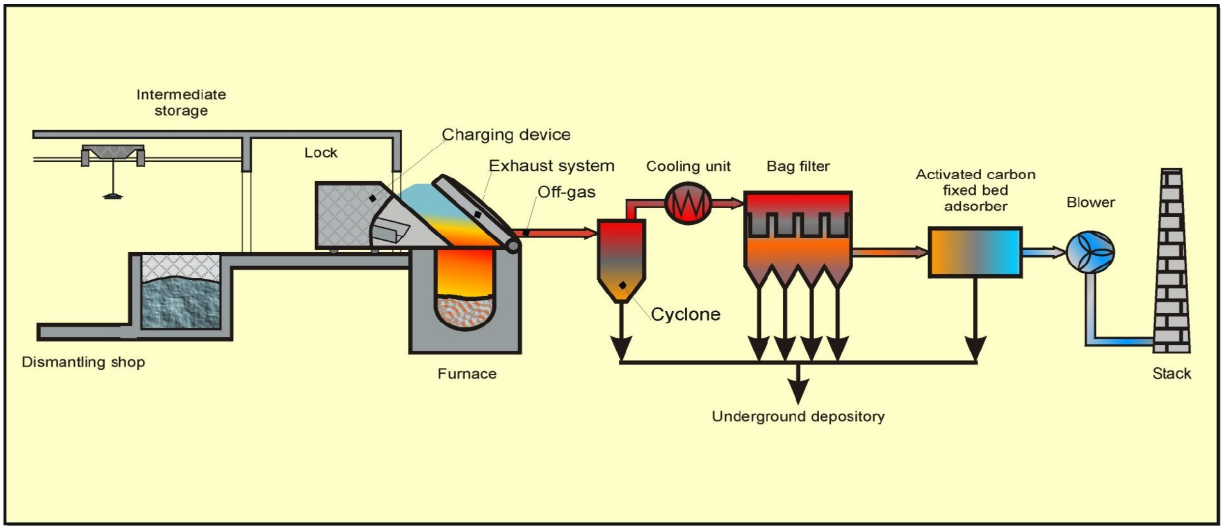

Figure 2: GERTA melting plant

Concerning the melting point of tungsten, Siempelkamp uses the eutectic (17-25 wt.-% tungsten, 65–75 wt.-% iron, 1-4 wt.-% additives) to be able to process the tungsten at temperatures between 1,450 – and 1,500 °C. [3]

During the melting process the W-Fe-Th-alloy is solved and the main elements and components behave in different ways:

The thorium and its daughter products are almost totally transferred into the slag which is gripped from the surface of the melt.

Tungsten (and Molybdenum) remain in the melt and are mostly transformed into carbides according to the high carbon content [4].

The output of the melting process is metal, slag and dust. While the weight distribution amounts to 90-95 wt.-% metal, 4-10 wt.-% slag and 1-2 wt.-% dust, the main nuclides of the thorium decay chain remain in the slag and are very quickly in equilibrium state with their daughter nuclides. Due to their short half life the daughter nuclides transferred into the dust are present only for a short time. The distribution of the nuclides is shown in table 1 [5].

Table 1: Distribution of different radionuclides after melting

Nuclide	Melt	Slag	Dust
U 238, U 235	1 %	98 %	1 %
Th 232, Th 234	< 1 %	> 98 %	1 %
Ra 226, Ra 228	-	98 %	2 %
Pb 210	-	7 %	93 %
Po 210	-	2 %	98 %

Besides radionuclides, organic impurities are totally destroyed or evaporated.

The transfer of the radionuclides into the slag results in a decontaminated melt, which is reusable. The produced ferro-tungsten (17-25 wt.-% W) is used as an additive for alloyed steel. Figure 3 shows typical Siempelkamp ferro-tungsten ingots and a detail of the structure of the alloy.

Figure 3: Ferro-tungsten ingots and detail of the metal structure

Handling of Slags and Dust: Licensing and Legislation

The slag is free of any toxic impurities but contains a certain amount of the thorium. The German Radiation Protection Ordinance postulates the monitoring of NORM-contaminated material according to appendix XI, §96 respectively §102, if the personal may exceed 1 mSv per year. To check this limit value, exposure calculations were carried out by an accredited radiological expert team and all possible paths of exposure for the waste disposal, from recycling to final disposal, were taken into consideration [6]. The calculation based on the assumption of 100 Mg slag production from NORM-contaminated scrap per year. Table 2 shows the results of the calculation. This is linked to the condition of blending the slag at a ratio of 1:4 with slag from the conventional foundry and using it as road construction material or surface near disposal. Since starting operation of GERTA melting plant, 100% of the slag could be recycled by this path.

Table 2: Nuclide specific activity limits for waste disposal

Nuclide	Specific Activity
U-238sec	87 Bq/g
Th-232sec	65 Bq/g
Ra-226+	99 Bq/g
Pb-210++	161 Bq/g

Only 1-2 wt.-% of the input-material is dust retained in the bag filter and in the cyclone. Both kinds of dust are mixed with quick lime and are then filled into storage drums. In other melting campaigns up to 1 wt.-% of mercury can be detected in the dust. The chemical contamination of the dust, in particular the content of mercury coming from different melting campaigns, prevents recycling, so the dust is blended with the lime and is firmly bound and sent to underground storage. Underground storage in rock salt mines up to a depth of 200 metres offers a disposal solution for hazardous waste in Germany, that has long been regarded as safe for the environment. Drums are stored and subsequently covered by layers of anhydrite and clay originating from salt refining. The remaining hollow space is filled with rock salt and each cavern is sealed hermetically.

The radiation exposure to the mine workers and to the public has to be less than 1 mSv/a. Additionally, the filter dust must not be radioactive in the sense of the former ADR regulation for transport, that means the total activity of Pb-210/Po-210 must be below 70 Bq/g.

Activity Measurements

The determination of the total specific activity of incoming material is most problematic. A direct measurement of the specific activity is usually not possible due to the different geometry and density of the material. A calculation of the specific activity related to the surface contamination or related to the measured dose rate is necessary.

A method, which is quite simple for measuring the activity of specific radio nuclides is gamma-spectroscopy. For this method, no chemical preprocessing is necessary before measurement. Only geometrical characteristics and the density of the sample are important to determine the activity. Siempelkamp uses two HPGe-detectors (**H**igh-**P**urity **Ge**rmanium) and an analysis software of EG&G Ortec. One of the detectors is equipped with a carbon window at the top. This allows the detector to measure gamma-energies down to about 5 to 6 keV, which is necessary for detecting the gamma-energy of Pb-210 at 46.5 keV with sufficient efficiency. For gamma-analyses, different calibrations such as Marinelli beakers and wipe tests are used.

Dose Measurements During Tungsten Thorium Melting Campaign

In comparison to U-238, the dose factor of Th-232 is a lot more than two magnitudes higher than Uranium. For that reason, special staff dose measurements were carried out in three different ways: local dose, personal dose and aerosol.

The local dose was measured with Thermolumineszensdosimeters (TLD) and the personal dose was measured with electronic dosimeters EDW150A from Graetz.

The TLD's were installed near to the workplaces and the measured results supply only an average dose for a work area. The weighted man value considers that on a shift the staff is present only several hours/minutes at the different working places. The results are listed in table 3 and show no significantly increased dose for the time while handling the contaminated scrap.

Table 3: Local dose rates during tungsten project

No.	Expos. Time	Furnace Contr. Panel	Scrap Bunker	Shear	Melting Shop	Exit Dismant. Facility	Weighted Man Value	Weighted Man Value
	[mSv]	[mSv]	[mSv]	[mSv]	[mSv]	[mSv]	[mSv]	[µSv/d]
1	201	0.00	0.07	0.09	0.05	0.02	0.042	0.21
2	180	0.09	0.20	0.07	0.07	0.07	0.098	0.54
3	186	0.07	0.04	0.04	0.04	0.05	0.054	0.29
4	188	0.07	0.11	0.06	0.06	0.06	0.070	0.37
5	141	0.30	0.06	0.00	0.00	0.00	0.130	0.92

Mean Value		0.107	0.095	0.051	0.044	0.039	0.08	0.47
Stand . Dev.		0.103	0.056	0.029	0.024	0.024	0.03	0.25

The EDW's for personal dose measurement were positioned at the front of the workers body, mostly aligned to the contaminated material. Figure 4 shows the measured dose for 15 workers, who mainly dealt with the material. The displayed doses are corrected by subtracting the background at Siempelkamp site and also show the average value (red line) for these workers and the responding standard deviation.

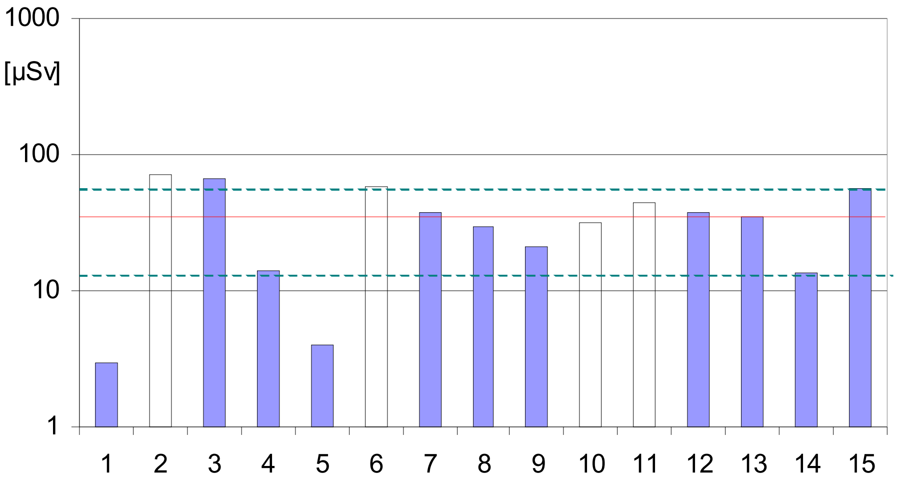

Figure 4: Personal dose of staff (15 persons) during tungsten project (background corrected)

The average dose during the whole project amounts to 35 µSv. Taking into account, that the measuring period was 30 shifts, an annual dose for handling exclusively this kind of material would be about 250 µSv.

Additionally to the personal dose measurements of the staff, aerosol measurements with an aerosol sampling device were carried out. The samples were taken at different workplaces, such as decanting and sorting areas of the delivered raw material and the operation area of the furnace. Table 4 shows the average values for the different operations and places.

Table 4: Average values of aerosol measurements

Operation/place	Ac-228* [Bq]	Pb-212* [Bq]	Act. conc. Ac-228* [Bq]	Ratio of Ac 228-based Decay chain to Pb-210 Based decay chain
Decanting of material	**12.1**	**20.1**	**0.2**	**0.6**
Furnace handling	**13.8**	**49.5**	**2.4**	**0.28**
Furn. exhaust syst.	**9.7**	**792.0**	**258.7**	**0.01**

* relates to the decay chain behind Ac-228, respectively behind Pb-212

The most significant dose risk, when working with thorium contaminated material, is incorporation. Especially inhalation of Th-232 and some of its daughters can cause a high organ- and effective dose. To check a possible incorporation of thorium, urinal tests of four persons of staff were made, that were directly in contact with the contaminated scrap and were measured using the HR-ICP-MS method.

It could be proved, a personal dust filter presumed, that the incorporated activity is less than minimum detectable activity by HR-ICP-MS method.

Conclusion

In 2002 Siempelkamp Nukleartechnik invented a process to decontaminate and reuse tungsten srap, which is alloyed with thorium-oxide.

The experience of melting 130 t of tungsten scrap has shown that:

- The scrap could be decontaminated and transferred into a marketable ferro tungsten product
- The slag is reusable according to the German legislation
- The process takes place far below the limits of dose exposure for workers and public from 1 mSv/a.

Literature

[1] U. Quade; W. Müller: Melting of Toxically and Radioactively Contaminated Scrap, Erzmetall 11/2002

[2] Ludwig, T.: Strahlenschutz bei Arbeiten mit thoriumhaltigen Elektroden, Strahlenschutzpraxis 4/2002

[3] Volkert, G.; Dautzenberg, W.: Durrer, Metallurgie der Ferrolegierungen, 2. Auflage, Springer Verlag,

[4] Internal study, Institut für Gießereitechnik, Düsseldorf, Dec. 2003

[5] U, Quade, W. Müller: Recycling of radioactively contaminated scrap from nuclear cycle and from natural sources, European Metallurgical Conference, Hannover, 16.-19. Sep. 2003

[6] U. Quade; S. Thierfeld; S. Wörlen: Release of residues from melting NORM contaminated steel scrap – a German approach. WM ´03, Waste Management Conference, Tuscon, AZ, USA, 23.-27. Feb. 2003

SOIL CONTAMINATION IN A RURAL SITE USED FOR RARE EARTH INDUSTRY BY-PRODUCT DISPOSAL

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Abstract

In the past the processing of monazite aiming production of rare earth elements was performed in São Paulo state. This industry produced large quantities of byproducts and wastes: cake II (uranium and thorium hydroxides) and mesothorium cake (Ba (Ra)SO_4). At that time the National Commission of Nuclear Energy – CNEN didn't have regulations for this kind of activities. At the moment CNEN is preparing regulations regarding NORM processing industries and also for intervention situations.

Between 1975 and 1981, 3500 tons of cake II was stored in seven rectangular concrete pits three meters deep, surrounded by 30 cm concrete walls and floor, which were built for this purpose in a country area of São Paulo state, a region of farms. A river flows across the property into the public water supply of a city, 12 km far from the site. Activity concentrations of ^{228}Ra varying from 0.5 to 50 Bq/g were identified in the soil by a preliminary survey, which indicates that the site was contaminated by radionuclides of the ^{232}Th series from the by-products and wastes. The inhabitants of the region are very concerned about the situation.

The purpose of this paper is to identify and characterize the extension of the contamination in the soil and to derive guideline concentrations with the goal of the site remediation. Besides, an assessment of public risk perception has been performed. This assessment will give support to introduce the public participation in remediation process and establish a work methodology, in order to obtain a more effective communication between regulator and society.

Introduction

The chemical processing of monazite performed by a Brazilian Industry has produced two radioactive residues: thorium concentrate cake, a by-product named cake II - average content 20% of thorium hydroxide and 1% of uranium hydroxides, specific activity around 1800 Bq/g and mesothorium - $Ba(Ra)SO_4$ - a waste with specific activity around 4400 Bq/g.

Approximately 3500 tons of cake II were stored in a site with an area of 283679 m^2. This site is located on a farm region which encircles a basin, streams of other declivities, eight wells and nineteen springs, which supply the local inhabitants (Figure 1). It is crossed by a brook that disembogues in a river supplying a big town 12 km away.

The cake was stored in seven rectangular 3.5 m deep pools with concrete walls fifteen cm thick. Each pool is one meter above the soil surface and 2.5 m underground. (Figure 2).

From 1975 to 1981, when the pools were filled there was a lack of national regulations on this kind of industrial residue. Neither radiological environmental impact nor geological studies were considered in the choice of the storage place. [1]

At the moment CNEN is preparing regulations regarding NORM processing industries and also for intervention in these situations.

In the past, the monitoring program performed by The Institute for Radiation Protection and Dosimetry IRD/CNEN showed values up to 4.0 Bq/L for ^{226}Ra, with average values of 0.1 Bq/L in a site well. [2] The same program has pointed out some soil contaminated areas, up to 70000 Bq/kg for ^{228}Ra, 890 Bq/kg for ^{226}Ra and 13000 Bq/kg for ^{238}U. [3]

This paper aims at presenting the actual status of this storage site and to discuss the preliminary results of the radiological soil characterization.

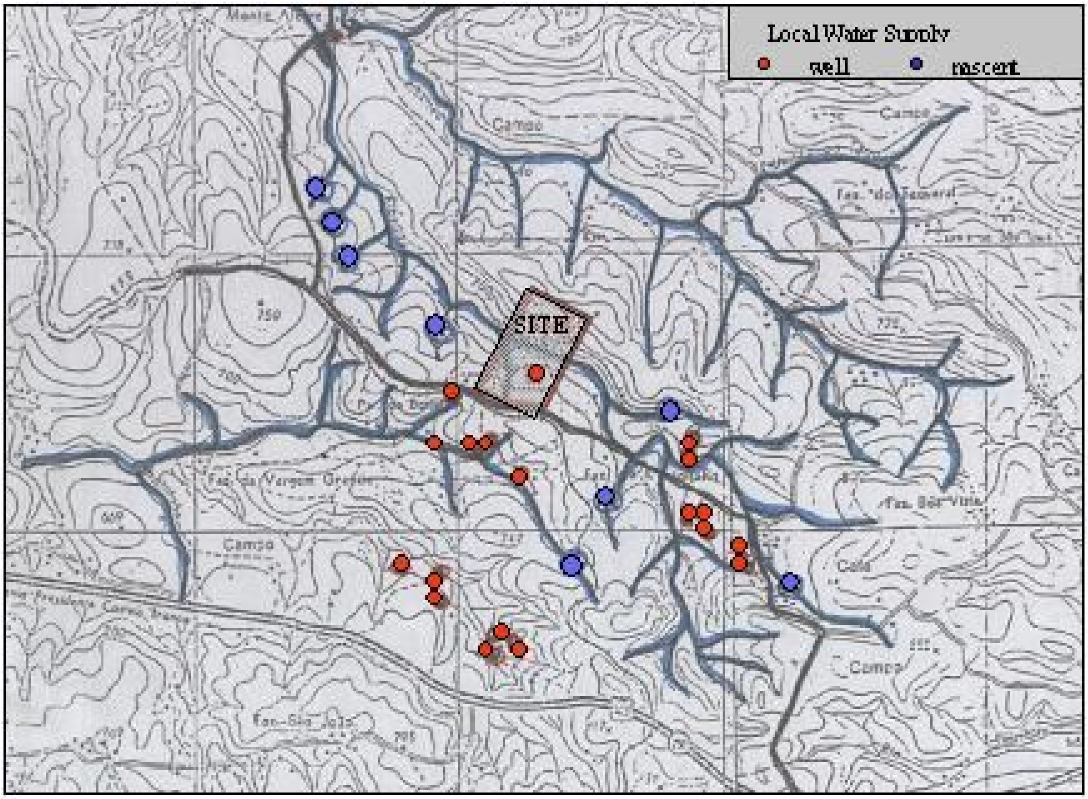

Figure 1: Diagram of Local Water Supply

Figure 2: Storage Concrete Pools

Methodology

According to MARSSIM methodology [4] the site was subdivided in 6 survey units, classed in impacted or not impacted, based on the historical site assessment. Four survey units (Figure 3) were defined as having higher potential for radioactive contamination: A, B, C, located around the pools and unit D, outside the storage area fence, in the slope of a hill, along the preferential direction of water flow.

In order to optimise the screening, a triangular grid system was applied to these units, as it is more efficient for locating small contaminated areas. (Figure 4) The distance among points of the grid was 11 meters and they were located with a theodolite. The number of data points, for each survey unit, calculated with the Wilcoxon Rank Sum Test [4] was 10. The same number was used to the non-impacted area (Area F), and low potential area (Area E). In these units, where no contamination was expected, the 10 soil samples were taken at random. Units A, B and C have approximately 2000 m^2 each. Unit D around 800 m^2 and unit E around 60000 m^2.

As a background reference, the region on the other side of the river was selected (Area F), clearly a non impacted area, with a forest undisturbed by human activities, and biological, chemical and physical characteristics similar to original environment of the site.

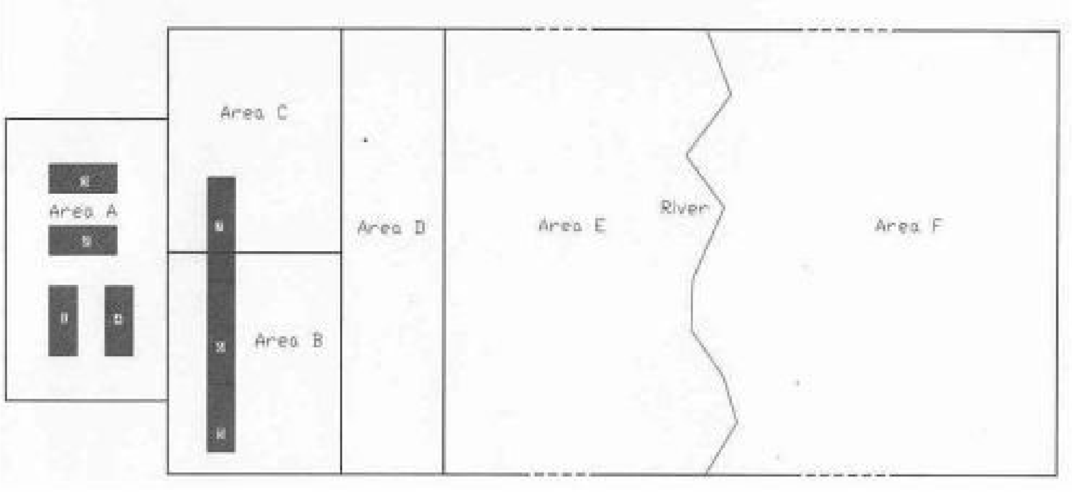

Figure 3: Soil Characterization Areas

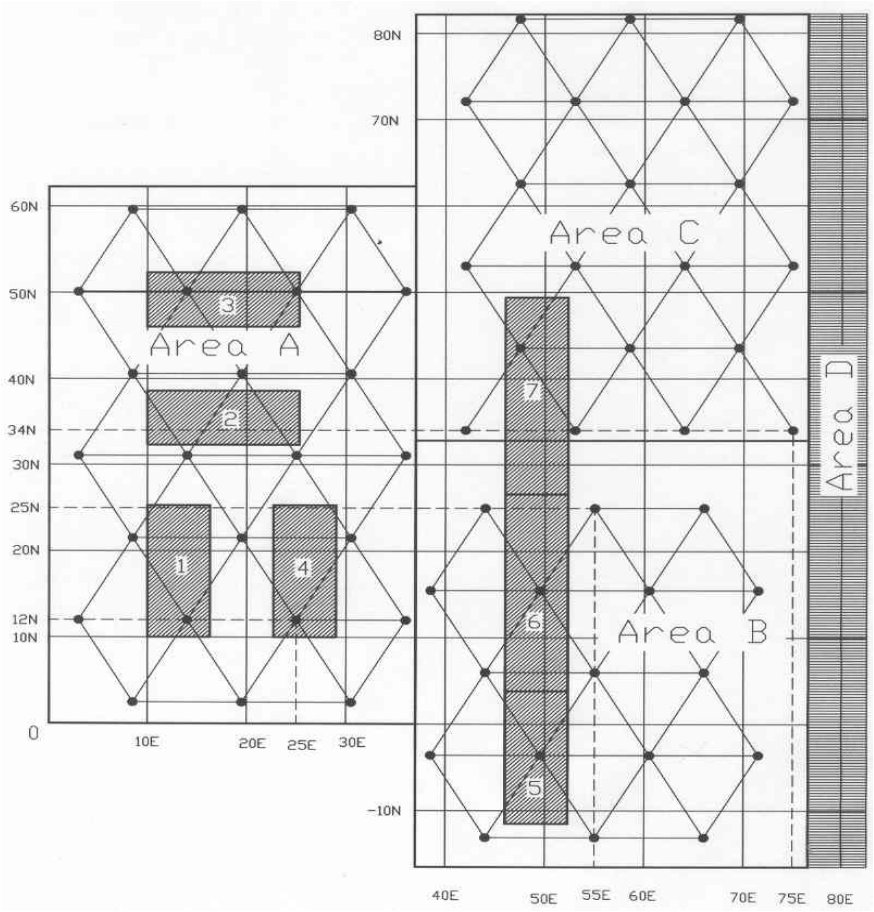

Figure 4: Triangular Grid Adopted to Determine Soil Samples Locations

In each point was collected soil at surface (15 cm) and subsurface (150 cm and 300 cm), each sample consists of two kilos, conditioned in plastic bags.

Results and Discussion

As the storage is a site derived from past practice, some information describing its complete history, from the start to present time, is lacking. The authors are still collecting information to accomplish the site historical assessment. The older facilities are far of today's legislation and must be fit in the new safety documentation requirements.

Conditions may have changed after the previous surveys, since allegedly the owner of the property removed 2 meters of superficial soil of the site. In this case, some hot spots pointed out by monitoring program measurements would no longer exist at surface soil, therefore the importance of this new site characterization.

The soil samples for background evaluation were analysed in a LEGe detector, model GL2020R, CAMBERRA. The background samples showed an average value of 39.2 Bq/kg for ^{228}Ra, being the highest value 58.8 Bq/kg and the lowest 17.3 Bq/kg.

Although the site characterisation is not complete, the preliminary results pointed out three hot spots in area A from 339 Bq/kg to 2965 Bq/kg for ^{228}Ra. In area D two hot spots were identified, showing values of 3650 Bq/kg and 3810 Bq/kg for ^{228}Ra, the latter being 97 times the average background. The samples from area B haven't been analysed yet. Area C presented two points with 274 Bq/kg and 712 Bq/kg for ^{228}Ra.

In the past, the radiological environmental monitoring program performed by São Paulo State Environmental Protection Agency - CETESB and CNEN showed, in a site well, values up to 4.0 Bq/L for alpha activity and 3.6 Bq/L for beta activity [2]. Other measurements in outside site wells showed values not higher than 0.08 Bq/L for Ra 226 and 0.01 Bq/L for Ra 228 which is considerable below the 2001 Ordinance of the Ministry of Health, which states the limits 0.1 Bq/L for alpha emitters and 1 Bq/L for beta emitters.

Up to the present time, the actual origin of contamination is still unknown, existing two possibilities to be tested:

- Storage site impact: fracture at the bottom of the pools due to worn down conditions from long time storage, causing radionuclides migration;
- Surface soil contamination occurred in the past, as a consequence of spilling that took place during the material transportation and filling of the pools eventually causing radionuclides migration to the water table.

Both cases have regulatory aspects associated: in the first case, lack of regulations to guide construction and safety evaluation of a previous activity to CNEN radioprotection standards, in the second case it must have been caused by poor training of workers. CNEN started regulating radiological occupational and environmental surveys after the site construction. Testing this hypothesis will be fundamental to support the decision making process about the site.

References

1. Garcia Agudo, E; Gonçalves, S.; Francisco, J. T.; Shinomiya, C. N. “The Use of Radium Isotopic Ratio in Groundwater as a Tool for Pollution Source Identification” in: Fourth International Conference Low-Level Measurements of Actinides and Long-Lived Radionuclides in Biological and Environmental Samples. Rio de Janeiro, Brazil, October 15-20, 1992.
2. Magalhães, M. H.; Zenaro, R.; Lauria D.C “The Radium Concentration in Groundwater at a Waste Disposal Site in Brazil. Is it a Naturally Occurring or a Contamination Process?” in Seventh International Symposium Natural Radiation Environment (NRE-VII), Rhodes, Greece, 2002
3. Nouailetas Y, Lauria D.C. et al “Radioecological Questions Concerning the Monazite Sand Cycle Wastes in Brazil” Radiation Protection in Australia, vol 11 (4), 177 – 181, 1993
4. NUREG 1575, NRC/EPA/DOE “Multi Agency Radiation Survey and Site Investigation Manual (MARSSIM)”, August 2000

STATUS OF RADON DOSIMETRY IN ZAMBIAN UNDERGROUND MINES

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Abstract

The Zambian economy has significantly relied on copper and cobalt mining in the relatively uraniferrous Katanga Basin with a potential hazard of radon for over 50 years now. The radon preliminary survey of Hayumbu et al (1998) showed that at least 30% of the 42 randomly sampled sites in 8 underground mines had radon levels over 1000 Bq/m^3 (IAEA, 1996).

This paper outlines on-going radon dosimetry activities in Zambian underground mines and presents radon grab sampling and personal measurements at one of the mines identified to have high radon concentrations during the preliminary survey.

Introduction

Mining is a global industry undertaken for its economic benefits of wealth creation and employment [1, 2]. In Africa, commercial-scale mining provides important benefits in terms of exports/foreign exchange earnings and tax receipts to nineteen African countries. One of these countries is Zambia where the sector contributes 80% of the exports, 10% of the GDP and 15% of total formal employment [3-5].

The above mentioned social-economic benefits of the mining industry notwithstanding, in developing countries, the industry is likely to be associated with three potential negative effects. The first one is the social-economic dislocation an ill-prepared mining community goes through at mine closure which arises from exploitation of a non-regenerative resource. The second and third undesirable aspects arise when inoptimal management of mining operations results in environmental degradation and/or negative health impacts on miners and surrounding communities. Principal health problems among miners from various countries that have been cited by the literature include respiratory diseases, neoplasms/cancers, injuries, HIV/AIDS (important studies in South Africa), chronic hypertension, mental health (often related to mine closure) and genetic impact (in the case of uranium) [1,2, 6,7].

Although silica has recently been identified as a carcinogen [8], the historical neoplasm/cancer hazard among miners is exposure to radon [9]. The suspicion that working in underground mines is associated with cancer goes as far back as the mid 1500s when Georgius Agricola wrote about the high mortality of miners in the Carpathian Mountains of Eastern Europe. Later autopsy studies of miners in the 1800s in that region demonstrated that chest tumors, later demonstrated to be primary lung cancer, were a common cause of death [10].

In the early 20th century, mines in the present Czech Republic were found to have high radon levels and researchers suspected that this exposure was the cause of the miner's lung cancer. In the 1950s, radiation scientists recognized that particulate radon progeny and not radon gas delivered the radiation dose ultimately responsible for causing cancer. Several epidemiologic cohort studies of radon-exposed underground miners with relatively high exposures during the 1950s and 1960s confirmed the association between radon exposure and lung cancer. The main cohorts that have been studied include uranium miners in Czechoslovakia, France, Canada, Australia and the US, fluorspar miners in Canada, iron miners in Sweden and tin miners in China. In Africa, radon measurements have not been as extensive as in developed countries. Measurements have been performed by countries such as South Africa, Namibia, Niger and Morocco which are well known for mining uranium or uranium rich phosphate ores.

This paper is on the status evaluation of the radon hazard in Zambian copper and cobalt underground mines in the relatively uraniferrous Katanga Basin with a potential hazard of radon. The radon preliminary survey of Hayumbu et al [11] showed that at least 30% of the 42 randomly sampled sites in 8 underground mines had radon levels over 1000 Bq/m^3 [12]. Work to map radon in Zambian underground mines following the preliminary survey started in mines with the largest number of sites with concentrations above 1000 Bq/m^3. Thus far, radon mapping has been performed at two mines. At the first mine, only radon area measurements have been done while at the second one, both area and personal measurements have been performed. This paper is on measurements at the second mine.

Experimental

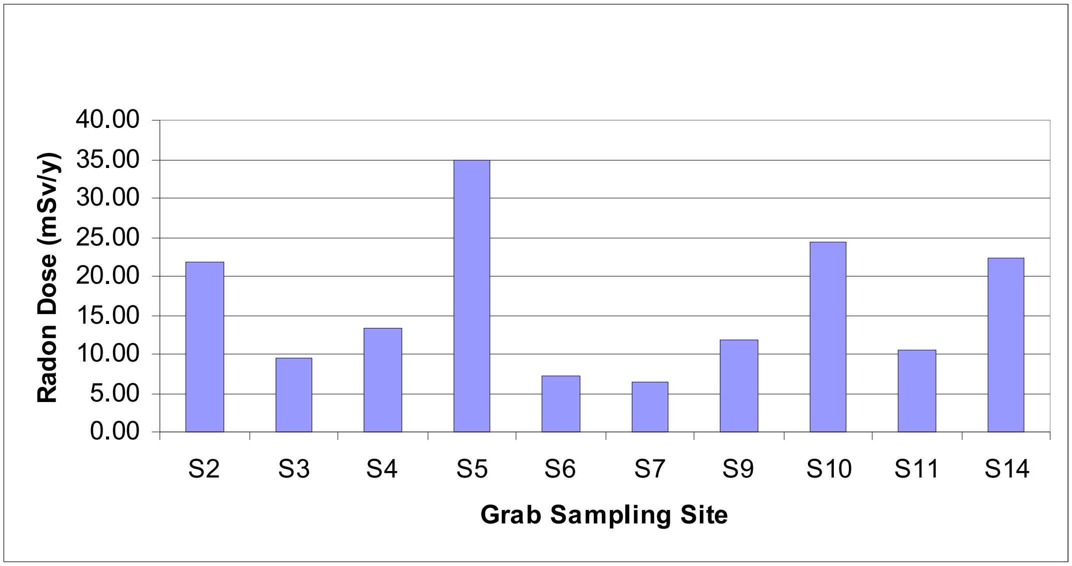
Radon area levels were measured using two methods. In the first method, field measurements of potential alpha energy concentrations (PAEC) of radon daughters (μJ/m^3) and equilibrium factors of radon and its daughters were made using a Pylon

Working Level (WLx) Meter. PAEC concentrations were directly converted to radon dose (mSv/y) for each site. In the second method, triplicate grab samples collected in Lucas Cells at field measurements sites were counted on a Pylon AB-5 Radiation Monitor to obtain radon concentrations (Bq/m^3) that were converted to mean site radon dose levels using the equilibrium factor. These area radon measurements formed a cluster of sites in one section of the mine in which personal radon dose of seven job categories were also assessed. Seven representative workers for each work category were given dosimeters using LR-115 integrating nuclear track detectors for a month. At the end of the month, detectors were sent to ALGADE in France for dose evaluation.

Results and Discussion

Results obtained for the two methods of area radon doses using grab sample and field measurements were comparable (R^2=0.9995). Figure 1 below shows a sample of area dose measurements in one section of the mine. These results show that all radon dose levels in this section of the mine are above the action limit for individual dosimetry (5 mSv/y) and some measurements are above the occupational exposure level of 20 mSv/y.

Figure 1: Radon Grab Sample Measurements of September 2002

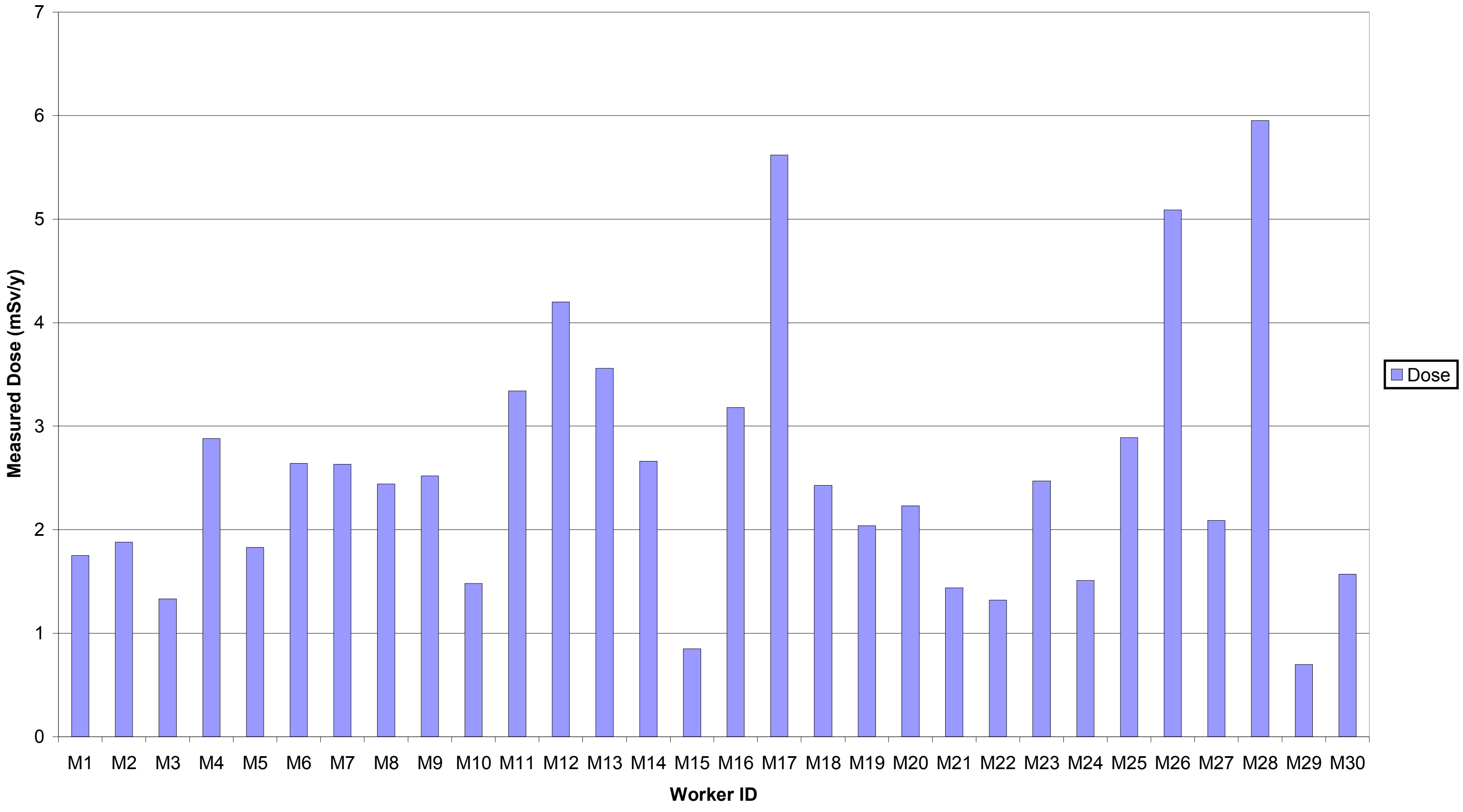


In exposure assessment, one flaw of area measurements is use of the assumption that a worker spends the whole year working at the site that have a radon dose level comparable to those at sampling sites of radon throughout the year. Correcting this flaw in our study entails taking measurements using personal samplers that provide radon levels integrated over a month. Figure 2 below shows personal radon dose measurements for workers operating in the work area previously characterized for area radon doses shown in Figure 1. It is apparent that personal doses are on average four times lower than area doses and no workers in this section of the mine have radon exposures that exceed the occupational exposure limit of 20 mSv/y.

Conclusion

Limited personal radon measurements thus far performed in Nchanga underground mine are a factor of four lower than area measurements and indicate that during this study no worker has received personal doses above the occupational exposure limit. Further, for this mine, processing of track detectors deployed to measure area doses is underway [13] so that the mine's radon map of area doses can be prepared. Mine-wide grab sample and field radon dose area measurements performed during deployment of track detectors show a similar trend in radon exposure doses shown in Figure 1. The map, when it is ready, will guide personal radon exposure assessment for the rest of the mine.

Figure 2: Radon Personal Measurements of September 2002 – June 2003



References

1. Mining, Minerals and Sustainable Development (MMSD) Report No. 210, Worker and community health and safety informal experts meeting: Workshop report, London, 10 September 2001, International Institute of Environment and Development (IIED), England, 2002, p4.
2. Mining Review Africa, The Green Mine, Issue 1, 2002, p20. http://www.miningreview.com/archive/021/20_1.htm, 03/10/2004.
3. Mbendi's E-mail Mining News, Zambia – Mining: copper mining – overview. http://www.mbendi.co.za/indy/ming/cppr/af/za/p0005.htm, 02/20/04.
4. Mining in Zambia, http://www.zambia-mining.com/miningright.html, 02/20/04.
5. Mulenga, S C, Konkola Copper Mines plc – Zambia: Contribution to poverty alleviation through sustainable development, KCM, Chingola, Zambia, December 2003.
6. WHO Prevention and control exchange, Hazard prevention and control in the work environment: Airborne dust, Geneva, Switzerland, WHO/SDE/OEH/99.14, 1999.
7. NIOSH, Work-related lung disease surveillance report 2002, Cincinnati Ohio, US Department of Health and Human Services, Public Health Service, Centers of Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No 2003-111, 2003.
8. IARC, IARC monographs on the evaluation of carcinogenic risks to humans: Silica, some silicates, coal dust and para-aramid fibrils. Vol 68. Lyon, France: World Health Organization, International Agency for Research on Cancer, 1997.

9. ICRP, Protection Against Radon-222 at Home and at Work. ICRP Publication 65. A report of a Task Group of the International Commission on Radiological Protection, 1993.
10. Frumkin, H and Samet, J M, Radon, Environ Carcinogenesis, 51(6), 2001, 337-344.
11. Hayumbu, P, Malikana, E M and Hussain, M M, Preliminary Survey of Radon Levels in Some Copper/Cobalt/Pyrite Underground Mines in Zambia, NISIR, Lusaka, 1998.
12. IAEA, IAEA Basic Safety Series No. 115, Vienna, 1996.
13. E. M. Malikana, Private communications, Ministry of Health, March 2004.

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IMPORTANCE OF SAMPLING IN RELATION TO THE GAMMA SPECTROSCOPIC ANALYSIS OF NORM AND TENORM MATERIAL

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Summary

This paper describes the developments over the past 25 years of low background gamma-spectroscopic analysis of NORM and TENORM materials to a state-of-the-art semi-automatic gamma analysis system. The developments were initiated in the early eighties of the last century in order to be able to measure low specific activities in fly ash samples. The developments involved modifications and improvements of commercially available hardware, auxiliary equipment, improvement and

development of analyzing software, correction software and processing software to a semi-automatic reporting of the analysis results.

The above summarized effort has lead to the following detection limits e.g. ^{238}U 3 Bq/kg, ^{235}U 0.3 Bq/kg, ^{226}Ra 5 Bq/kg, ^{210}Pb 30 Bq/kg and for ^{40}K 60 Bq/kg by a measuring time of 70000s of a specially tuned gamma spectroscopy system for NORM and TENORM materials.

These low detection limits show the need to set up representative sampling procedures for NORM and TENORM materials. It is not be possible to define a sampling procedure that will be valid for all types of sampling. Therefore it is advised that in the case that it can be expected that sampling have to be performed at regular times to set-up and validate a sampling procedure for the materials dealing with. The procedure has to be based on an existing national or international standard.

1 Introduction

In the Netherlands problems arose with naturally occurring radioactive materials (NORM) and technical enhanced concentrations of NORM (TENORM) in the early eighties of the last century. This was due to discussions about the reuse of fly ash in building and road construction materials [1]. A gamma spectroscopic analysis of NORM and TENORM samples was at that time still in its infancy. Nowadays different gamma spectroscopic analyses techniques exist all with their specific accuracy. Today’s state of the art techniques are able to assess the specific activity of uranium and thorium chains present in the variety of NORM and TENORM material with an accuracy of about 3%. This means in practice that the error due to sampling of NORM material has become and will be more and more important by the radiological characterization of samples of NORM and TENORM materials. This importance has been also increased by the implementation of the EC directive L159 in the national legalisations of the European Community member states.

The main aim of this paper is to give an overview of the improvements achieved in the last decades -technical as well as procedural- that have lead to the state of the art gamma spectroscopy analyzing techniques for NORM and TENORM materials.

The second aim is to provide information about how to set-up representative sampling of NORM and TENORM materials in practice, in order to increase sampling accuracy and by this increasing the overall accuracy.

2 Gamma spectroscopic analysis

The development of gamma spectroscopy systems as a tool for the non-destructive analysis of materials started in the early days of the nuclear industry and was further developed for the analysis of activated materials. Due to the relative simplicity of the technique it has become one of the most widespread analyzing tools used for the assessment of the specific radioactivity of materials.

A distinction has to be made between “low-resolution” and “high-resolution” gamma spectroscopy systems. Generally low-resolution gamma spectroscopy system are equipped with a NaI(Tl)-detector or more general the applied detector has a full-width-at-half-maximum (FWHM) of more than 6% at 661 keV. These low-resolutions systems are suitable for the analysis of radioactive materials emitting a single or a few well-separated gamma energies. In the case of NORM and TENORM materials, due to high number of gamma energies NaI(Tl)-detectors are less suitable and will therefore not further be taken into account. High-resolution gamma spectroscopy systems are in general equipped with a semiconductor detector.

The first wide scale commercial available semiconductor detectors for high energy gamma photons were Ge(Li)-detectors (see figure 1). Almost directly detectors were commercial available with active volumes of about 45 cm^3 and a FWHM between 5-10 keV for ^{60}Co [2].

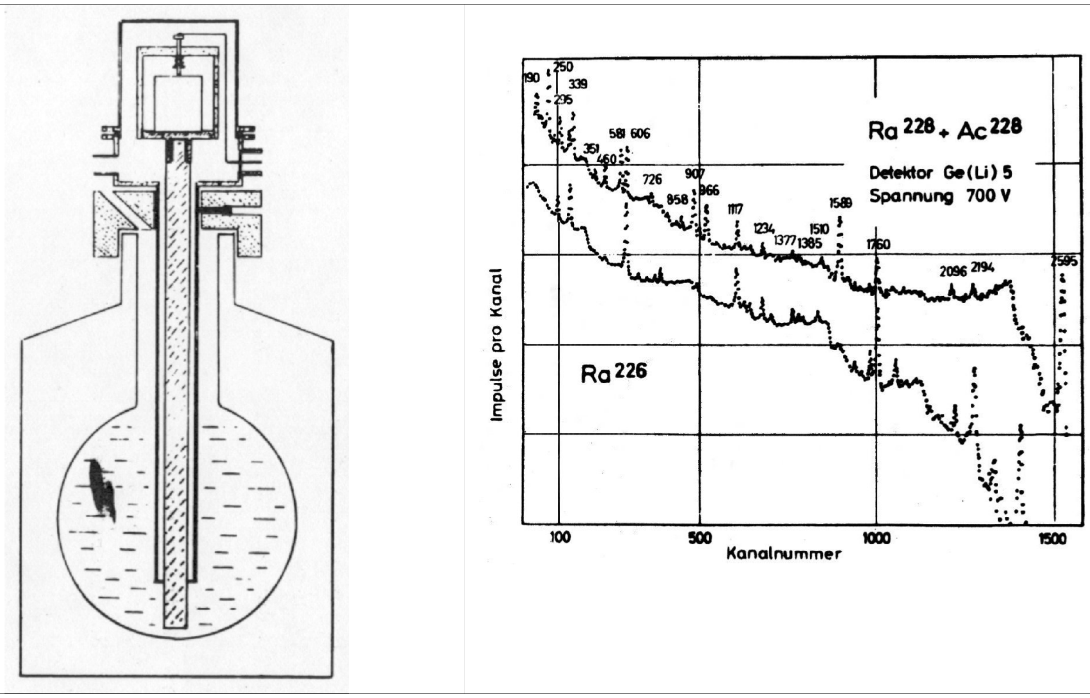

Figure 1 **Schematic diagrams of a semiconductor detector fabricated in the year 1967 and a recorded gamma spectra of ^{226}Ra and ^{228}Ra including daughters [2].**

As stated before in the Netherlands problems arose with NORM and TENORM materials in the early eighties of the last century and this was mainly due to the reuse of fly ash in building and road construction materials. At nuclear department of KEMA, as predecessor of NRG, knowledge and experience were present at that time [3] to start the development of a very low background semiconductor gamma spectroscopy systems [4] in order to be able to measure accurately the specific radioactivity of the fly ashes. In the following years a large number of possible improvements have been investigated and the most beneficial are implemented, of which some are nowadays generally accepted and applied. The improvements concern:

- Construction materials applied by the manufacturing of the detector.
- Construction of the detector.
- Shielding of the measuring cavity.
- Flushing of the measuring cavity with gasses.
- Calibration.
- Sample geometry.
- Software.

Construction materials applied by the manufacturing of the detector

To decrease the intrinsic background of the system a program was started to measure the specific activity of all used construction materials [5]. The method specified by Capponi e.a. was followed [6]. As an outcome of this program it was decided to start a selection procedure to obtain construction materials with non or as low as possible specific radioactivity. Especially the replacement of aluminum by other materials like magnesium and stainless steel decreased the total specific activity of the detector.

Construction of the detector

The standard end cap of the detector was replaced by an extended cap so that the pre-amplifier could be placed outside the measuring cavity and shielded. From the above mentioned measuring program it was found out that the molecular sieve contains a relative high specific activity. This activity was shielded for the detector by placing a cylindrical block of aged lead around or into the cold finger.

Shielding of the measuring cavity

To decrease the measuring time and to be able to reach the required very low detection limits the special lead shielding had to enclose a cavity large enough for a 4-liter Marinelli beaker. This meant, that the cavity had to have at least a cylindrical shaped space with a height of 320 mm and a diameter of 550 mm. The shielding of the measuring cavity has to be multi layered and consisting at all sides of at least -starting from the outside- 100 mm common lead, but selected on low specific activity, 10 mm of aged lead manufactured at least 300 years ago, 2 mm of cadmium and 10 mm of low specific active copper.

Flushing of the measuring cavity

From nature the nuclides ^{222}Rn and ^{220}Rn are present in air. Both radon isotopes are continuously emanated from the soil and by the present building construction materials. The concentration in the air is low and equilibrium will be established due to radioactive decay. The contribution to the background by ^{222}Rn and ^{220}Rn and daughters is substantial and this is due to the small “source-detector distance”. However, this equilibrium strongly depends on local meteorological and geological circumstances. This means that the equilibrium can quickly change in time and this causes that also the background can vary quickly. To establish a stable background in first instance filtered air was pumped into the measuring cavity preventing environmental air entering the cavity by the small over pressure (see figure 2). However, this method did not fulfill all expectations especially on the long term. Therefore, the measuring cavity is now flushed with nitrogen and is cleaned at a regular time interval with alcohol. All plastics are removed from the cavity (plastics become static on the long term and accumulate short radon decay products).

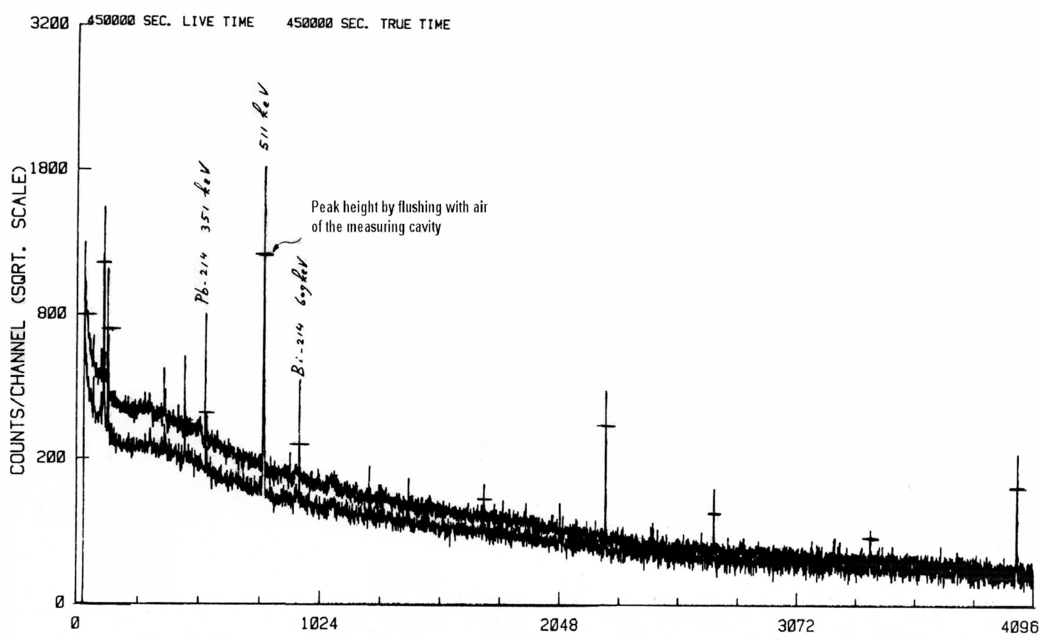

Figure 2 Influence of flushing the inner space with filtered air on the background.

By taking of the above mentioned measures into account the background can substantially reduced as can be seen from table 2.

Table 1 Overview of achieved backgrounds for some photon energies reported in literature.

Photon energy [keV]/(no. systems)	Maximum [counts/ks]	Minimum [counts/ks]	Median [counts/ks]
185/(9)	15	<0.006	0.3
239/(16)	8.9	<0.005	0.77
352/(12)	17	<0.1	2.2
511/(9)	19	0.25	10

583/(14)	6	<0.002	0.62
609/(16)	5.8	<0.003	0.77
911/(12)	1.1	<0.001	0.18
1461/(18)	4.4	0.008	1.05
2615/(14)	2.5	<0.001	0.51

Calibration

Due to the fact that gamma spectroscopy analysis had its origin in the nuclear industry and activation research with a wide variety of radionuclides that the calibration of these systems is mainly “energy” instead of “nuclide” orientated. Energy depended calibrations are therefore become the most widespread calibrations and are described in national and international standards [7,8]. The advantage of an energy over a nuclide depended calibration is that identification of an unknown photon peak is relatively easy, but the disadvantage is that to correct for coincidence and summing are difficult to perform. Samples coming from the nuclear industry such as from cooling systems or environmental monitoring programs are well defined and will not vary much in density or in composition in time. For this reason it is rather easy to manufacture a calibration source that matches these samples, so that no actions have to be performed to correct for the self-absorption of photons in the sample. This is not valid for NORM and TENORM samples. These samples can of course be chemically and/or physically treated in such a way that they match a standard calibration source. However, the disadvantage is that those samples will not be any longer in their original state and cannot be used for follow up analyses. Furthermore it is evident that each step of a chemical or physical treatment has to be verified and that these treatments will decrease the overall accuracy and will increase the routine analyze costs.

Table 2 Advised nuclides to be applied by an energy depended calibration of high-resolution gamma spectroscopy systems. For NORM and TENORM analysis the list has to be extended with the nuclide ^{210}Pb.

Nuclide	Photon energy [keV]
^{241}Am	59.5
^{133}Ba	81.0
^{109}Cd	88.0
^{57}Co	122.0
^{203}Hg	279.2
^{133}Ba	356.0
^{137}Cs	661.6
^{54}Mn	834.8
^{88}Y	898.0
^{60}Co	1173.2
^{60}Co	1332.5
^{40}K	1460.8
^{88}Y	1836.0
^{210}Pb	46.5

In the case of NORM or TENORM samples coincidence and summing corrections can be performed under the condition that the exact absolute efficiency for the entire energy range is known. E.g. without coincidence corrections it is not possible to calculate the contribution of ^{235}U in the 186 keV photon peak. Therefore it is advised to perform a new calibration as soon as a sample differs from the applied calibration source. At NRG as a rule of thumb “a new calibration has to be performed when the analyst assesses that the density and/or chemical composition of the sample differs more then 5% from the calibration source”. It is unambiguous that there are so many combinations of density and chemical compositions possible that fulfill this rule of thumb and that it will become an impossible job to create physically all calibration sources needed. Therefore NRG has set-up R&D projects to develop experimental methods to assess in routine the self-absorption behavior of samples for different photons energies [9,10] and software that is able to calculate absolute efficiency curves for every unique sample [11-14]. The developed software code is a semi-empirical Monte Carlo program able to calculate the relative differences between a unique sample and the applied calibration source. The software needs as input a geometry description of the detector crystal and sample. Both inputs can be sufficiently descended from the manufacturers specifications. The code has been validated extensively in house [15] and by participation in an international comparison exercise [16]. By the above-described developments an accuracy of better then 4% could be achieved for the ^{226}Ra and ^{228}Ra chain and for ^{210}Pb better then 8%. However the accuracy for ^{238}U and ^{235}U were still depending and influenced by physical properties of the unique sample and varied from 5% up to 10%. This accuracy could not be reduced further mainly due to the fact that by taking into account coincidence and summing corrections not only the accuracy of the absolute value of the specific activity but also the uncertainty of the value increased [17].

To overcome this problem investigations were performed with “nuclide” dependent calibrated gamma spectroscopic systems, because this type of calibration has in principle less problems with coincidence corrections. Nuclide depending calibrations were performed for each of the natural radionuclides of interest. Calibration samples have been prepared directly form certified materials or indirectly by application of know amounts of certified tracer solutions onto aluminum oxide powder [18]. By applying the developed technique for calculating calibration factors per unique sample an accuracy of better then 5% could also be achieved for ^{238}U and ^{235}U.

Software

The analyzing software has to be able to combine the different nuclide depended calibrations. At this moment no commercial available software package can perform this is a sufficient way. Therefore the final calculations are performed in a special developed Excel spreadsheet in which the results of the gamma spectroscopy analysis are used as input. In this Excel spreadsheet the results of different energies belonging to a single radionuclide are statistically weighted and outliers are removed. This approach improves the accuracy of the measurement result and decreases the uncertainty at the same time.

Sample geometry

It is evident that the sample geometry has a direct influence on the absolute efficiency and the minimum detection limit. In the case of samples taken from low specific activity NORM material that can be expected to be in secular equilibrium, large volume samples can be measured e.g. in Marinelli beakers on P-type high-purity germanium detectors. However in the case of TENORM samples it is advised to measure smaller samples up to 100 cm^3 that can be placed directly on top of a N-type high-purity germanium detector (N-type HpGe-detectors are more suited for measuring photons below 60 keV then P-type HpGe-detectors). This is due to the fact that by TENORM samples ^{210}Pb can be expected not to be in secular equilibrium with the remainder of the natural uranium decay series and its emitted photon has an energy of 46.5 keV. Photons of 46.5 keV are not able to pass the construction materials of the sidewall of the HpGe-detector end cap.

3 Representative sampling

The result of gamma spectroscopic analysis of NORM and TENORM samples define often the follow-up actions for all the material the samples represent. The current national legalisations of European member states are based on the EC directive L159 [19] and is in general more stringent than former legislation if any with regard to NORM, with as a direct consequence that the financial costs of follow-up actions will increase.

Existing state of the art gamma spectroscopic systems can provide some compensation. However, due to the fact that at this moment sampling is mostly not performed according national or international standards, the accuracy determined by a gamma spectroscopic analysis will be and often *has to be* decreased by an assessed accuracy based on the performed sampling. This assessed accuracy will be in general (much) larger then the determined accuracy of the gamma spectroscopic analysis.

This means (see also table 1) that at this moment, when analysis are performed with a state of the art system, the most benefit with regard to the overall accuracy of the results can be gained by means of improving the sampling procedures.

It is not possible to define a general procedure valid for all types of sampling. This can be concluded directly from the large number of different sampling procedures described in the various national and international standards. The list of available standards is extensive and it looks like there is a standard for every topic. Besides this, defining such a procedure will not give you any guarantee that governmental agencies and inspectorates will accept the developed sampling procedure.

Therefore the approach to establish a representative sampling according to a validated procedure has to be pragmatic, meaning:

- Select out of available standards the two or three most appropriate standards. The search for applicable standards should not be limited to national standards or to standards applied normally in your industrial activities. E.g. select out of national standards and ISO-standards.
- Compare these standards and make a (draft) note. In this note the following has to be unambiguous: Which standard is the most applicable, which has to be accompanied by an in dept motivation.
- Test the selected standard e.g. validate the standard for your NORM or TENORM material(s).
- Finalize the note, including results of the performed validation.
- Send an official request with the final report to involved governmental agencies and inspectorates to agree on that the selected standard is applicable for your NORM or TENORM material(s).

It is evident that such an approach will have the largest benefit as soon as it becomes clear that sampling has to be performed at a regular base. The sampling can deal of coarse with raw bulk materials, scales of tubes, sludge's, liquid etc. It is also evident that informing involved governmental agencies at an early stage and during the different stages will facilitate the decision making.

4 Discussion and conclusion

Gamma spectroscopy is an efficient and powerful tool to measure the specific radioactivity in samples taken from NORM as well as TENORM material. In table 3 a schematic overview of parameters is given indicating their influence on three important properties of a gamma spectroscopy system e.g. background, detection limit and accuracy.

Table 3. Schematic overview of parameters that influence the background, detection limit and accuracy properties of a gamma spectroscopy analysis.

Parameter description	Background of the system	Detection limit	Accuracy
Applied materials in the detector	+	+	-
Construction of the detector	+	+	-
Efficiency of the detector	-	+	+
Shielding of the measuring cavity	+	+	-
Flushing of the measuring cavity with gasses	+	+	-
Calibration	-	-	+
Sample geometry	-	+	+
Specific activity of the sample	-	+	+
Measuring time	-	+	+
Software	-	-	+
Sampling	-	-	+

By setting up such a specialized tool for analyses of NORM and TENORM samples the following aspects have to be taken into account:

- Selection of HpGe-detector. Samples taken from NORM material that can be expected to be in secular equilibrium can be measured with a P-type detector. However this type of detector is not suited for measuring TENORM material. Therefore it is advised to perform such measurements at a low background N-type detector.

- Measuring cavity. The shielding surrounding this cavity has to be made of materials selected on their specific radioactivity and has to be multi-layered as described above to optimize its background reduction. The cavity has always to be flushed with nitrogen and no plastics are allowed.
- Calibration. The best analysis results will be obtained by “nuclide” dependent calibrations of the system in combination with software that is able to calculate the unique self-absorption correction per sample. The accuracy of this software has to be better then 7 % for photons from 40 keV up to 100 keV and better then 4% above 100 keV.
- Analyzing software. This software has to be able to combine the different nuclide dependent calibrations.
- Sample geometry. There are no volume restrictions for samples of NORM materials that are in secular equilibrium. This is in principle also valid in the case of samples of TENORM materials, however due to the fact that the nuclide ^{210}Pb is the restricting nuclide, samples with a volume of 100 cm^3 will be in general sufficient.
- Accuracy. For obtaining the most accurate results from NORM and TENORM samples, samples have to be kept locked gastight for a period long enough to establish the radioactive equilibrium between ^{226}Ra and its daughters (e.g. 3 weeks). During the preparation of the samples attention has to given to the lock-up procedure, because free space is not allowed above the samples. The nuclide ^{222}Rn will otherwise not stay homogenously distributed inside the sample.

With a gamma spectroscopy system equipped with a N-type HpGe-detector having a relative efficiency of 25% that incorporates also the above mentioned innovations the following detection limits can be obtained for ^{238}U 3 Bq/kg, ^{235}U 0.3 Bq/kg, ^{226}Ra 5 Bq/kg, ^{210}Pb 30 Bq/kg and for ^{40}K 60 Bq/kg by a measuring time of 70000s. It is evident that detection limits depends on the total activity of a sample.

These low detection limits show also the need to set up representative sampling procedures for NORM and TENORM materials. It will not be possible to define a sampling procedure valid for all types of sampling. Therefore it is advised that in the case that it can be expected that sampling have to be performed at regular times set-up and validate a sampling procedure for your materials based on an existing national or international standard.

Literature

1. Van der Lugt, G.; Gamma spectroscopic analysis of thorium, uranium and radium in coal and fly ash; KEMA 83-16 MO-Rad; February 1983.
2. Kemmer, J.; Aufbau eines hochauflösenden Gamma-Spektrometers und Beispiele für seine anwendung. Halbleiterdetectoren in Strahlenschutz und Strahlenmesstechnik, Jülich Mai 1967 p146.
3. Van der Lugt, G., e.a.; Plan of approach for the removal of the buried radioactive waste of the KEMA property; KEMA 10638-80 Rev 1; November 1980.
4. Kiezenberg, W.H.T., Scholten, L.C.; Development of low background gamma spectroscopic systems. KEMA 84928-RSS 87-5007; June 1983.
5. Scholten, L.C., Van der Lugt, G.; Determination of the own specific radioactivity of a GeLi-detector; KEMA 79-78 MO-Rad; October 1979.
6. Capponi, M., Massa, I., Piccinini, M.; Monte Carlo simulated detector responses to gamma radiations coming from extended sources. Nucl. Instr.& Methods 217 (1973).
7. NEN 5623; Radioactivity measurements – Determination of the activity of gamma ray emitting nuclides in a counting sample by semiconductor gamma spectroscopy.
8. NVN 5629; Radioactivity measurements – Determination of the activity of gamma ray emitting nuclides in a counting sample by means of low gamma spectroscopy using a NaI(Tl) detector.
9. Romeijn, S.; Theoretical approach of the mass attenuation coefficient of an arbitrary material; KEMA November 1993.

10. Kuipers, M.G.; Determination of the average atomic number of an arbitrary material with the aid of transmission measurements; KEMA June 1997.
11. Van Velzen, L.P.M.; Calculation of the absolute efficiency of a unique sample; KEMA 40343-NUC 93-5083; July 1993.
12. Van Velzen, L.P.M.; Monte Carlo calculations of gamma ray absolute efficiency factors for volume sources; Proceedings Portsmouth 1994 IRPA Congress on Radiological Protection.
13. Kiezenberg, W.H.T.; Investigations on calibration methods for gamma spectroscopy; KEMA 40919-NUC 95-9095; November 1995.
14. Van Velzen, L.P.M.; Calibration methods for Marinelli beakers; KEMA 41259-NUC 96-9194; October 1996.
15. Van Velzen, L.P.M.; Semi-empirical Monte Carlo Program for virtual calibrations of gamma spectroscopy systems; General program information & User manual; NRG March 2000.
16. Lépy, M.C., e.a.; Euromet action 428: Transfer of Ge detectors efficiency calibration from point source geometry to other geometries; CEA report CEA-R-5894; February 2000.
17. Debertin, K., Helmer, R.G., Gamma- and X-ray spectrometry with semiconductor detectors, par 4.5 Coincidence summing corrections; Atomic and Nuclear data. Elsevier Science Publishers B.V., Amsterdam, 1998.
18. Van Weers, A.W., De Groot, T.J.H., Analytical aspects of NORM from oil and gas production and processing. Proceedings NORM 1, Amsterdam September 1997.
19. Eurotom 96/29; Council directive of 13 May 1996 laying down basic safety standards for the health protection for the general public and workers against the dangers of ionizing radiation; OJ L-159 of 29 June 1996.

FACTORS CONTROLLING MEASUREMENTS OF MASS RADON EXHALATION RATE

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Abstract

The mass radon exhalation rate of soil samples was measured using a tight emanation chamber of 10 dm^3 of volume and Lucas cell. The results showed that the mass of sample, grain size fraction and water content influence the radon mass exhalation rate. For the soil of a radium activity of about 2500 $Bq{\cdot}kg^{-1}$, at the sample mass of the interval from 0.20 kg to 0.50 kg, the values of the mass radon exhalation rate are higher than that at the other sample masses. The dependence of the measured exhalation rate on sample mass supposedly can be explained by a heterogeneous distribution of radon atoms in the air space of the emanation chamber and an enlarging of sample dimensions due to the mass increasing. The observed radon exhalation rate decreased with the enlarging of grain sizes and it intensively increased at the water content at a few percent by weight, then decreased with the moisture growth. Due to these influences the measured values of the mass radon exhalation rate should be reported together with the data of the physical parameters of the sample material.

Keywords: Mass radon exhalation rate; Sample mass; Grain size; Moisture

1. Introduction

A part of radon and its progenies in the entire natural radioactive dose is above 50% [Porstendorfer, 1993], so a problem of mitigation of radon concentration in the room air from day to day has become more important. To do it one should investigate the radon exhalation rates of the building materials. One of the kinds of radon exhalation rate is a mass one. The determination of the mass radon exhalation rate is based usually on the measurement of a growth rate of radon content in the air in a tightly closed emanation chamber containing the sample of the investigated material. The procedure seems to be simple, however the measured results for the same material differ in a wide range [Neznal, 2001]. To find a ration for this ambiguity, the authors have examined the influence on the measurement results of such factors: the mass sample, grain size fraction and moisture of the investigated material.

2. Measurement method

To measure the mass radon exhalation rate, an emanation chamber of a volume of 10 dm^3 (20x20x25 cm) and a Lucas cell coupled with an electronic apparatus AB-5 (*Pylon electronic*) were used. An investigated sample of a known physical parameters such as: mass, volume and moisture was placed in the tightly closed emanation chamber. Fig.1 presents a view of the measurement stand. It shows that the Lucas cell was connected with the emanation chamber by the plastic pipes and valves. The connecting system enabled the air in the measurement system to be moved only from the emanation chamber to the Lucas cell and the other way round. In order to shield the radon progenies from the emanation chamber to the Lucas cell, in the entering way to the Lucas cell there was a filter paper. Then radon content in the air chamber was measured every day. The radon content in the air chamber was measured until it had reached a saturation value. This measurement can be described as follows: Pumping the air from the emanation container to Lucas cell by the AB-5 pump for a time interval of 10 min., then 3 h after pumping stop, the pulse counting cycle was started. One cycle consisted of at least 6 times of pulse counting, each of them lasted for 10 min. The radon content in the Lucas cell $N_L(t)$[Bq] at the pumping stop moment t (t – interval of time from the moment of the closing of emanation chamber to the pumping stop) was calculated by the formula (follow Pylon Instruction):

$$N_L(t) = \frac{\sum_{i=1}^{n} \frac{NCP_i \cdot C}{3 \cdot 600 \cdot \varepsilon \cdot A_i}}{n} \qquad (1)$$

Where NCP_i is a count rate of i-th time of pulse counting less background in counts for 10 min., ε – counting efficient, n – the number of pulse counting times (in the case n equals to 6). C and A_i are the correction factors for decay during the counting interval (in the case it was equal to 10 min.) and time interval between Lucas cell pumping stop and start of i-th time of pulse counting respectively. The values of the coefficients C and A_i can be found in the *Pylon Instruction* [Pylon instruction, 1989].

The number of 3 in the formula (1) is connected with the fact that after 3 hours of the pumping stop the radon in the Lucas cell is in equilibrium with its two alpha radioactive daughters. The radon content in emanation chamber at the pumping stop moment $N_C(t)$ was calculated:

$$N_C(t) = \frac{N_L(t) \cdot V_C}{V_L} \qquad (2)$$

Where V_C and V_L are the volumes of the emanation chamber and Lucas cell respectively.

A typical curve describing the growth of radon content $N_C(t)$ in the emanation chamber is presented in Fig.2. It can be expressed by an equation:

$$N(t) = a(1 - \exp(-bt)) \qquad (3)$$

Where: $b=\lambda$ - radon decay constant and the mass radon exhalation rate $E_m = (a \cdot b)/m$, where m is a sample mass [kg].

3. Influence of some factors on the mass radon exhalation rate

To investigate the influence of some sample parameters on the mass radon exhalation rate, a certain soil has been taken for the making samples of difference parameters. The soil was in grain form of difference sizes; its concentrations of ^{226}Ra, ^{232}Th and ^{40}K were measured through a gamma spectrometry and amounted to 2560 ± 30 [Bq/kg], 73 ± 2 [Bq/kg] and 443 ± 12 [Bq/kq] respectively.

3.1. Sample mass

In order to investigate the mass influence on the mass radon exhalation rate, some samples of difference masses have been made from the mentioned soil. For each sample, the mass radon exhalation rate was measured by the described method.

Table 1 presents the masses, volumes V_S of samples and adequate measured mass exhalation rates E_m. The dependence of E_m on sample mass m is presented on Fig.3. The view of the curve of the dependence can be supposedly explained by:

- Heterogeneous distribution of radon atoms in the space of the emanation container due to gravitation effect.
- Enlarging of the sample dimensions due to the increasing of its mass.

Due to gravitation effect, the majority of escaped radon atoms place in the surrounding near the soil sample. Therefore, if the sample mass is small, so its volume is too small in the comparison with the chamber volume, more radon atoms surround near the sample and less atoms in the other places. The fact can cause the decreasing of the measured radon exhalation rate. If the mass of the sample is too big, the sample dimensions become too large, so a certain part of the emanated radon atoms could be confined to the sample. So in consequence the appearance radon exhalation rate could be smaller than should be.

3.2. Size fraction

For purpose of the investigation of the grain size fraction influence on the mass exhalation rate, 4 samples of grain size: less than 1 mm, from 1 mm to 2 mm, 2 mm to 4 mm and larger than 4 mm were created by a sorting of above mentioned soil. In the sample where the grain sizes are greater than 4 mm, it was confirmed that there were some grains of maximum diameter equal to 8 mm. The mass of the sample of the grain sizes of the interval of 1mm to 2mm was the smallest and it amounted to 200 g, therefore the masses of 3 other samples were chosen to be equal to 200g. Fig. 4 presents a relation between the measured radon mass exhalation rate and grain size fraction. One can expect that the radon exhalation rate should be decreased with an enlarging of grain size [Markanen, Arvela, 1992], this fact is due to decreasing of total surface area of the all grains of the measured sample, so it could cause the decreasing of emanated radon atom number. However the phenomena is not entirely visible on Fig.4. The fact could be connected with both a possibly different distribution of radium atoms on the size fractions and the big enough deviations of the measured results.

From the Fig.3 and Fig.4 one can notice that the average value of the measured exhalation rates for the samples of the mix size grains is higher than that for the samples of the sorted size grains. The fact is due to the higher porosity for the samples of mix size grains than that for the other ones.

3.3. Sample moisture

To make some samples of difference moisture, first 3 kg of investigate soil has been dried at the temperature of 105 °C until its mass had been not changed. Then 4 samples of 0,5 kg of mass were made from the dried soil. To have 4 samples of water contents of 0%, 2%, 6% and 10 % by weight the water of mass of 10.2g, 32g and 55.5g were added to the second, third and fourth sample respectively. Then each sample was measured by the described method. The measured results are presented on the Fig.5. It shows that at first the radon mass exhalation rate increased with water content enlarging, reached the maximum value at the certain value of moisture and then decreased with water content increasing. The fact can be explained by a target phenomena [Porstendorfer, 1991; Markkanen, and Arvela, 1992; Przylibski, 2000; Bossew, 2003]. If the soil is dry, a certain part of radon atoms originated from radium decay on the mineral surfaces due to high enough ejected energy (ca 83 keV) could pass through the pores (if the pores are small enough) and they stick to other minerals. So smaller radon atoms could be in the pores and the exhalation rate should be small. If the soil is moist, the radon atoms could be caught through the water in the pores and they could move out the sample. It causes that more radon atoms are in free air, so in consequence the radon exhalation rate could be increased. If the soil is wet - there is a lot of water. The water can cover the mineral surfaces and it leads to smaller radon atoms in air pores. So the radon exhalation rate could be small again.

4. Conclusion

The mass radon exhalation rate (E_m) depends on the measurement conditions and on the physical parameters of investigated materials. The dependence of E_m on the sample mass and the volume ratio V_S/V_C is explained by the heterogeneous distribution of exhaled radon atoms in the chamber and the decreasing of relative part of exhaled radon atoms due to increasing of the sample mass. E_m decreases with enlarging of grain sizes. The shape of the curve of the relation between exhalation radon rate and water content in the investigated material is explained by the target phenomena. Therefore we propose that one should give the radon mass exhalation rate together with the physical parameters of investigated material sample.

5. References

- Porstendorfer, J. (1993). Properties and behavior of radon and thoron and their decay products in the air. Proceedings of *"Fifth International Symposium on the Natural Radiation Environment*". Tutorial Session, Luxembourg Belgium, 73-139.
- Neznal, M. (2002). Materials of European Intercomparison Measurement of mass radon exhalation rate of building materials, Czech Republic, September 19-20, 2002.

-Pylon Instruction, (1989). Instruction manual for using Pylon ® Model 110A and 300A Lucas cells with the Pylon AB-5. Pylon Electronic Company, Canada.

-Markkanen, M. and Arvela, H. (1992). Radon emanation from soil. *Radiation Protection Dosimetry, 45*, 269-272.

-Przylibski, T.A. (2000). Estimating the radon emanation coefficient from crystalline rocks into groundwater. *Applied Radiation and Isotopes, 53*, 473-479.

-Bossew,P. (2003). The radon emanation power of building materials, soils and rocks. *Applied Radiation and Isotopes, 59*, 389-392.

Table 1.

Mass sample [kg]	V_S[dm^3]	$E_m \pm 2\sigma$ [Bq.s^{-1}kg^{-1}]
0.05	0.057	185 ± 15
0.10	0.140	189 ± 12
0.20	0.273	209 ± 8
0.35	0.412	215 ± 7
0.50	0.570	212 ± 6
0.70	0.800	175 ± 8
1.00	1.130	168 ± 4

Table 1. The mass, volume of the samples and adequate measured exhalation rates.

Figure 1. The view of the measurement stand

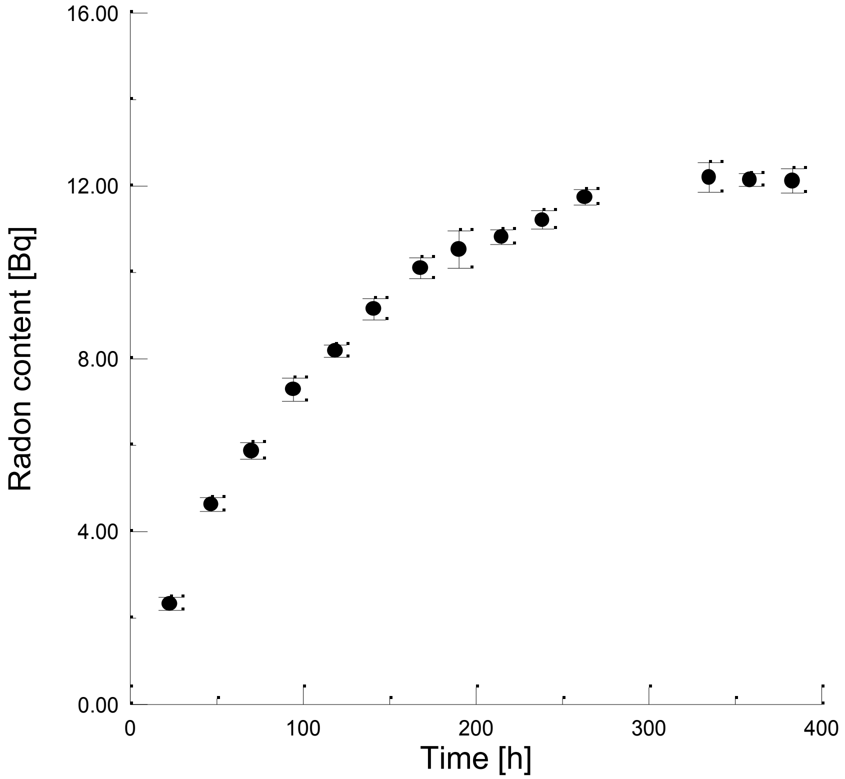


Fig. 2

Figure 2. The typical observed curve of the radon content growth in the tightly closed emanation chamber containing a investigated sample

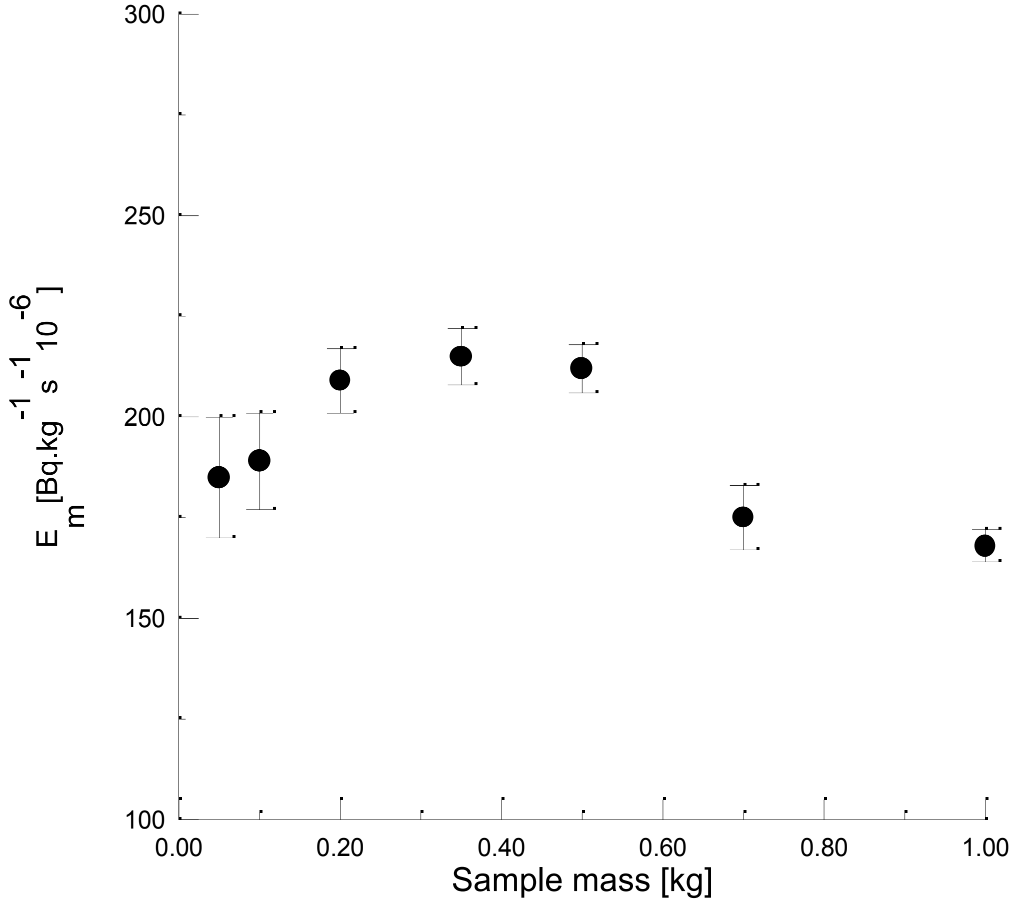


Fig.3

Figure 3. The measured radon mass exhalation rate as a function of the sample mass

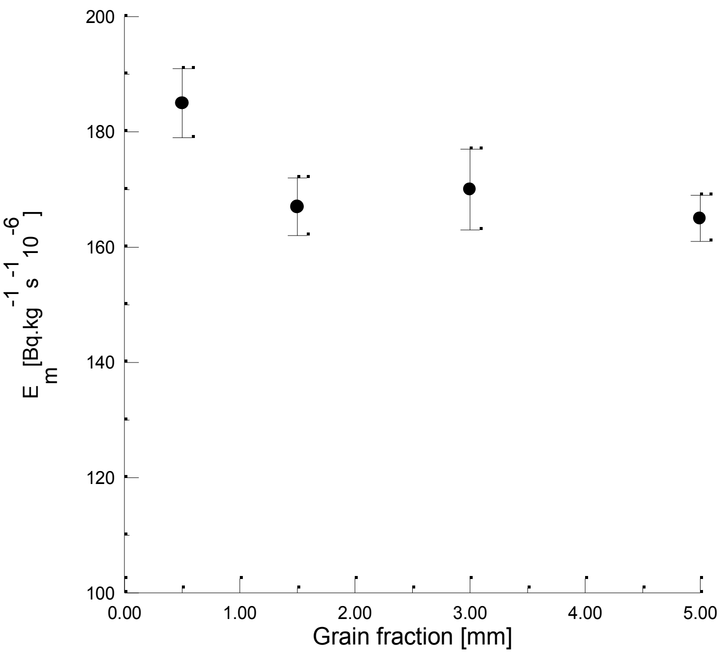


Figure 4. The measured radon mass exhalation rate as a function of the grain size fraction

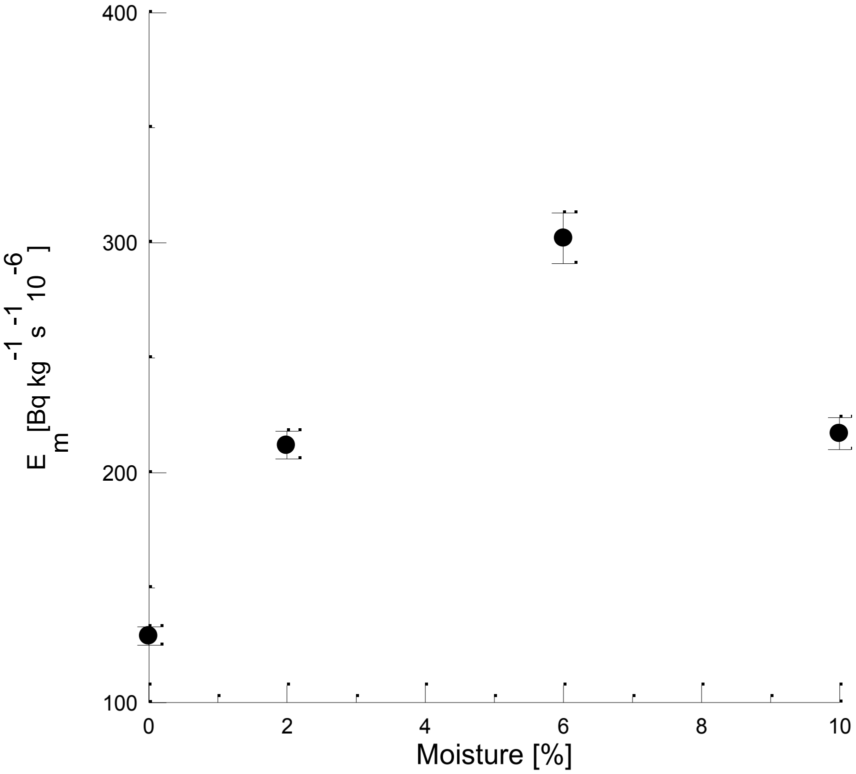
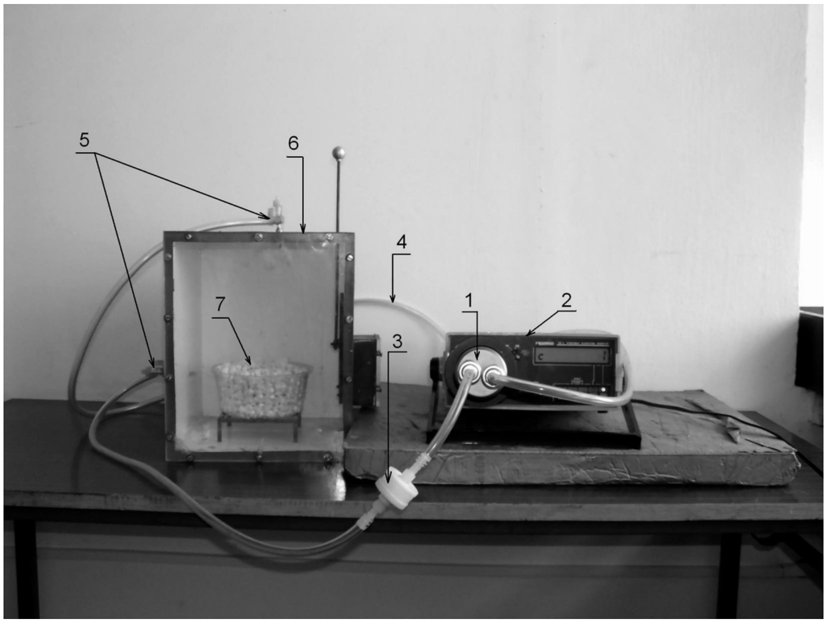


Fig.5

Figure 5. The measured radon mass exhalation rate as a function of the water content of the sample material.



CONCENTRATIONS OF ^{222}RN IN GROUNDWATERS FLOWING THROUGH DIFFERENT CRYSTALLINE ROCKS:AN EXAMPLE FROM ŚLĘŻA MASSIF (SW POLAND)

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ABSTRACT

Ślęża Massif is situated in the south-western part of Poland, about 30 km SW of Wrocław, the capital city of Lower Silesia. The geological setting of the research area is typical of the Sudety Mountains. Different types of crystalline rocks, both of igneous and metamorphic origin, occur on the area of 25 km^2. On the surface of this relatively small area, Lower Carboniferous to Lower Permian Strzegom–Sobótka Granite and Devonian Ślęża Ophiolite are uncovered. The result is the occurrence of granites, gabbros, amphibolites and serpentinites, directly neighbouring on each other.

The author selected this area for determining the influence of rock type on the concentration of ^{222}Rn dissolved in groundwaters flowing through crystalline rocks. The first stage of the research consisted of determining typical values of ^{222}Rn concentration in groundwaters flowing through different types of rocks and describing the scale of seasonal changes in ^{222}Rn concentration. In the next stage of the research, an attempt to apply ^{222}Rn as one of the isotopic hydrogeochemical tracers of pathways flow of fissure groundwaters will be undertaken.

The results show that the highest values of ^{222}Rn concentration (reaching 229 Bq/dm^3) were observed in groundwaters flowing out of springs located within granite, whereas the lowest one (1.1 Bq/dm^3) was noted in a spring located within serpentinite. The average ^{222}Rn concentrations obtained in groundwaters flowing out of two springs within granite were 170 and 103 Bq/dm^3, whereas the average values in two springs located within amphibolites reached 7.3 and 8.2 Bq/dm^3. The average ^{222}Rn concentrations in the springs flowing out of gabbro and serpentinite amounted to 7.6 Bq/dm^3 and 1.2 Bq/dm^3 respectively. ^{222}Rn concentration in the groundwater flowing out of the spring located within serpentinites was stable during the whole year, likewise the discharge of the spring. ^{222}Rn concentrations between 1.1 ± 0.2 and 1.4 ± 0.2 Bq/dm^3 were measured. On the other hand, ^{222}Rn concentrations in waters flowing out of springs located within granite were characterized by distinct changes. The highest values (164 and 229 Bq/dm^3) were noted in winter and in summer respectively, whereas the lowest ones (70 and 127 Bq/dm^3) were recorded in spring. There is no distinct correlation between radon concentration and the discharge of the springs. In the remaining springs, radon concentration changes were of low scale but also of irregular character.

The obtained results prove the necessity of precise location of groundwater intakes in the areas with complicated geological structure due to the need to ensure radiation security of local people. They also point to a possibility to employ radon (^{222}Rn) as a natural radioactive tracer of pathways flows and mixing zones of different components of underground and surface waters.

INTRODUCTION

The concentration of radon (^{222}Rn) in groundwaters depends on numerous factors, the most important of which are the emanation coefficient of reservoir rocks and the content of radium isotopes (^{226}Ra), the parent isotopes of radon, in these rocks. The concentration of ^{226}Ra in rocks is strictly related to the geochemical environment of their formation, hence also with the petrological type of the rock. In the study of radon hydrogeochemistry, it is important to become familiar with the relationship between the concentration of ^{222}Rn dissolved in groundwaters and the type (lithology) of their reservoir rocks. This is especially significant in areas built of crystalline rocks (magmatic and metamorphic), which usually contain higher ^{226}Ra concentrations than sedimentary rocks and more frequently undergo brittle deformations, producing favourable conditions for fast migration of radon and groundwaters. The greatest diversity of radon concentrations in groundwaters can be expected in areas with complicated geological setup and a large proportion of crystalline rocks. Conducting research in such an area may enable producing significant hydrogeochemical observations related to the occurrence of radon dissolved in groundwaters. This information could be later applied both for radiological protection and isotopic hydrogeological studies employing ^{222}Rn as a natural radioactive tracer of processes occurring in groundwater reservoirs. The best area for conducting this kind of investigations in Poland, due to the geological structure, are the Sudetes. They contain rather small zones characterized by very complicated geological setup in a relatively small area, which could be treated as natural proving grounds. One of such grounds is Ślęża Massif, whose another advantage to the author is its small distance from Wrocław, the capital of Lower Silesia.

GEOLOGICAL SETTING

Ślęża Massif lies in SW Poland, within the geological structures of the Sudetes, in their part lowered tectonically in the Tertiary, on so-called Fore-Sudetic block (Fig. 1.). Ślęża Massif is built of rocks belonging to two tectonic units of the western Sudetes. These are Lower-Carboniferous – Lower-Permian granites intruding into the epimetamorphic rocks of the Kaczawa metamorphic unit, forming the granite massif of Strzegom – Sobótka. In the SE, these granites come in contact with the largest Devonian ophiolite complex in Poland, so-called Ślęża ophiolite, built chiefly of gabbros and serpentinites.

On the selected proving ground, acidic igneous rocks (granites) and basic gabbros, metamorphic serpentinites and metadiabases, as well as metabasalts, formerly referred to as amphibolites, occur on the surface or under a relatively thin cover (Fig. 1.). Measurements of radon concentrations were conducted in spring waters flowing out of all the mentioned rock types. These are fissure and rubble springs, which can be all counted among slope springs. Their location has been also presented in Fig. 1.

MEASUREMENTS

The measurements of radon concentration in the spring waters of Ślęża Massif started in late autumn 2002, and are still proceeding. Together with every measurement of ^{222}Rn concentration, the temperature of water, its electrolytic conductivity (ECW), pH value, the total of dissolved solids (TDS), and the spring discharge are measured. All these measurements are conducted directly in the field, with the use of a conductometer and a pH-meter manufactured by SLANDI™, only ^{222}Rn concentration is determined in a laboratory. To do this, four 0.33-dm^3 water samples are taken from each spring, each into glass bottles secured tightly with a plastic cap. After being transported to the laboratory, the water is transferred, with a 0,1 dm^3 syringe, to an AquaKIT™ measurement set, which is connected to an AlphaGUARD™ portable radon monitor. As a result of air movement in the measurement set, forced by a gas-tight AlphaPUMP™, radon is released from the water in the AquaKIT™ system and transported to the ionisation chamber of the AlphaGUARD™ meter, where the proper measurement takes place. The values of ^{222}Rn concentration in the air obtained in this way are then converted into the concentration in the examined water sample by means of a computer programme AlphaEXPERT™, as well as with algorithms allowing concentration conversion at the moment of sample taking. A more detailed description of this measurement method can be found in numerous publications, including Przylibski & Adamczyk (2003), Przylibski (in press) or Przylibski et al., (in press).

RESULTS AND DISCUSSION

The measurement results have been compiled in Tab. 1. A relatively small number of data collected so far does not allow a full analysis of the changeability of ^{222}Rn concentration in the waters of particular springs. Therefore, it is not possible to determine potential correlations between the changes of the measured parameters. To do so, measurements are being continued in all springs. Nevertheless, the number of produced results enables drawing first conclusions about the range of value changes in the radon concentrations registered in the groundwaters flowing out of particular types of reservoir rocks. The unquestionably lowest values are characteristic of the waters flowing out of serpentinites ("źródło Życia", "Life spring"). What is also very distinct is the absence of seasonal variations in the measured radon concentrations, which change practically within measurement error limits, between 1,1 and 1,4 Bq/dm^3. Another characteristic of this spring is the constant discharge value (cf. Tab. 1).

The highest values of radon concentrations were measured, as expected, in the waters flowing out of granites ("Jasne" and "Korzenne" springs). In "Jasne" spring, they vary from 127 to 229 Bq/dm^3, while in „Korzenne" spring – from 70 to 164 Bq/dm^3 (cf. Tab. 1.). Radon concentration changes are high, although there are no regularities in their character. The maximum in "Jasne" spring was recorded in summer, at low spring discharge, while in "Korzenne" spring, it was in winter , at high discharge.

Similarly irregular changeability of ^{222}Rn concentration was observed in the waters flowing out of gabbros and amphibolites (metadiabases and metabasalts), but the values were much lower in comparison to those in the waters flowing out of granites and higher than those in the waters flowing out of serpentinites (cf Tab. 1). Radon concentrations in the waters of "Jakub" spring (flowing out of gabbros), as well as "Lustig" and "Joanna" springs (flowing out of metadiabases and metabasalts), oscillate between 6,5 and 10,5 Bq/dm^3. Changes in the concentration of this gas in the waters of the abovementioned springs have much a smaller amplitude compared with the waters flowing out of granites in "Jasne" and "Korzenne" springs.

Table 2 presents the extreme and mean concentration values of ^{222}Rn dissolved in the groundwaters flowing out of different types of crystalline reservoir rocks of Ślęża Massif. In spite of the still incomplete analytical material, distinct differences in the recorded values are observable between waters flowing out of granites and serpentinites, in relation to all the remaining rock types. At the same time, radon concentrations recorded in the waters flowing out of metadiabases, metabasalts and gabbros do not differ from each other, although they are different from those in the waters flowing out of granites and serpentinites (cf. Tab. 2). Lack of differences between ^{222}Rn concentrations recorded in the waters flowing through gabbros and those flowing through metadiabases and metabasalts results from the geochemical similarity of the environments in which these rocks were formed (especially with reference to U and Ra content). A similar geotectonic position – the zone of midocean rift – also did not help to diversify these rocks regarding their geochemical composition, as they were probably formed in the same magmatic reservoir.

Based on the presented investigation results, a statement can be made that even in a small area (e.g. within the distance of about 200 m – „Jakub" spring and „Jasne" spring, cf. Fig. 1), in regions with complicated and diversified geological setup, one can expect considerable differences in the concentration of radon dissolved in groundwaters. It is essential to recognise such a situation accurately while making plans for supplying water to the residents of such areas. In view of radiation security, the location of intakes should be planned very carefully in such cases. The knowledge of the value range of ^{222}Rn concentrations registered in the waters flowing out of (and through) different types of reservoir rocks is also of great importance for the possible use of radon as a natural tracer of pathways flow and the mixing zones of different components of underground and surface waters. The results of the still continuing research in Ślęża Massif, and other parts of the Sudetes, (Przylibski, in press) will form a basis for such an application of radon, occurring in groundwaters in different concentrations, depending on the type of the reservoir rock.

CONCLUSIONS

The results of the investigations into the concentration changes of ^{222}Rn dissolved in the groundwaters flowing out of springs in Ślęża Massif confirmed their dependence on the type of reservoir rock. The highest and simultaneously the most changeable values were recorded in the waters flowing out of granites, while the lowest values, exhibiting no significant variations in time, are characteristic of the waters flowing out of serpentinites. The measurements of ^{222}Rn concentrations dissolved in the groundwaters of this region make it possible to distinguish the waters flowing through granites and serpentinites from those flowing through the other rock types. On the other hand, groundwaters flowing through gabbros, metadiabases and metabasalts do not differ with regard to the concentration of radon dissolved in them.

The investigation results obtained so far point to the necessity of careful location of groundwater intakes in the areas with complicated (mosaic-like) geological setup, like the Sudetes, in order to ensure the radiation security of the local residents.

The presented results of the research carried out in Ślęża Massif, as well as in other parts of the Sudetes, suggest the possibility of employing radon as a natural radioactive tracer of pathways flows and the mixing zones of different components of underground and surface waters.

REFERENCES

Gaździk J., 1957 – Detailed geological map of the Sudetes. Scale 1 : 25 000, sheet Sobótka. Instytut Geologiczny, Warszawa. (in Polish).

Przylibski T. A., in press – Radon. The specific component of medicinal waters in the Sudety Mountains. (in Polish).

Przylibski T. A., Adamczyk A., 2003 – A new stand for measurements of ^{222}Rn concentrations in water in the Hydrogeological Laboratory on Mining Department at Wrocław University of Technology. Prace Naukowe Instytutu Górnictwa Politechniki Wrocławskiej, Nr 103, Konferencje Nr 36, „Zagadnienia interdyscyplinarne w górnictwie i geologii" III Konferencja Doktorantów, Szklarska Poręba, 24-26 stycznia 2003, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, ss. 329-343. (in Polish).

Przylibski T. A., Mamont-Cieśla K., Kusyk M., Dorda J., Kozłowska B., in press – Radon concentrations in groundwaters of the Polish part of the Sudety Mountains (SW Poland). Journal of Environmental Radioactivity, 2004, Vol. 74.

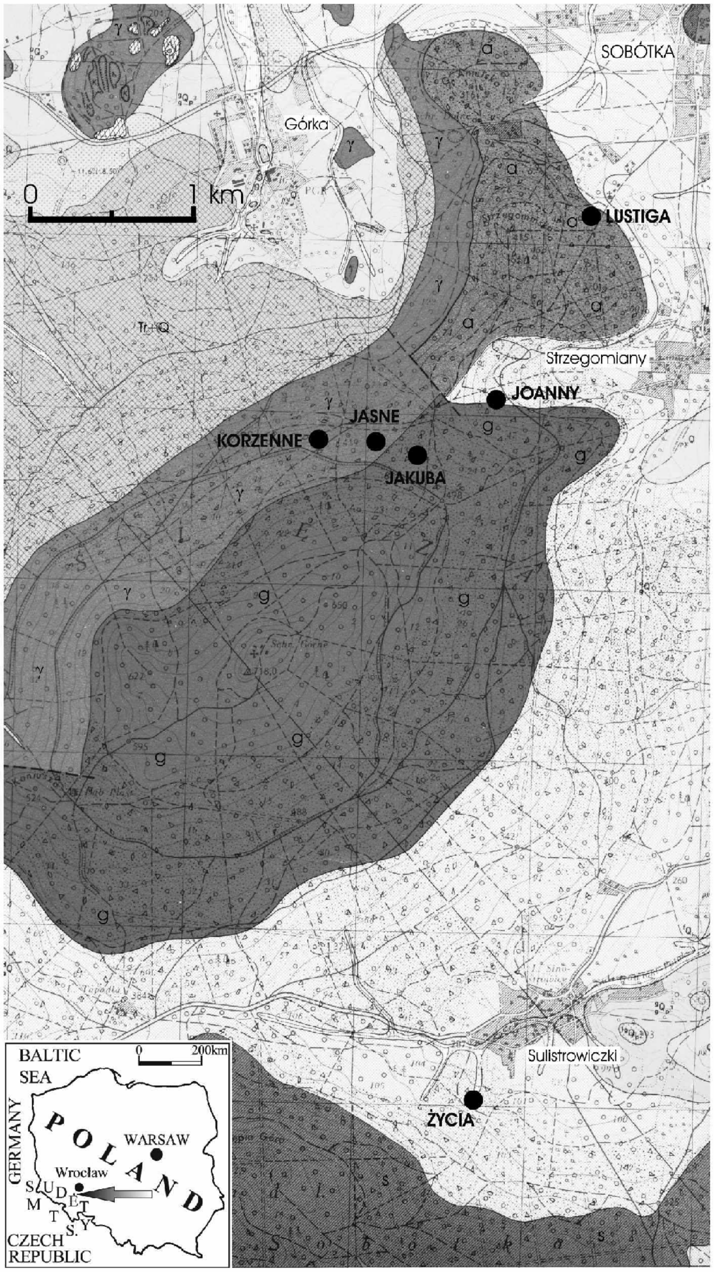

Fig. 1. Geological sketch of Ślęża Massif (according to Gaździk, 1957) with plotted springs in which ^{222}Rn concentrations were determined.

s – serpentinites (Devonian), a – amphibolites (now referred to as metadiabases and metabasalts) (Devonian), g – gabbros (Devonian), γ – granites (Upper Carboniferous), Tr+Q – granite waste rock (Tertiary and Quaternary), Q – clays, sands and gravels of the Quaternary;

black circles show spring location, the arrow on the map of Poland – position of Ślęża Massif.

Tab. 1. Values of parameters measured in the spring waters of Ślęża Massif flowing out of different types of crystalline reservoir rocks.

Spring	Date of sampling	Concentration of ^{222}Rn	Discharge		Temperature	ECW	TDS	pH	Type of reservoir rock
		[Bq/dm^3]	[dm^3/min]	[m^3/h]	[ºC]	[S/m]	[ppm]		
Życia	26.11.2002.	1.3 ± 0.3	13.3	0.80	10.0	375			serpentinite
	23.01.2003.	1.1 ± 0.3	13.8	0.83	9.9	412			
	19.03.2003.	1.2 ± 0.3	13.6	0.81	9.9	394	276		
	20.05.2003.	1.2 ± 0.3	13.6	0.81	10.0	394	276	7.81	
	16.07.2003.	1.1 ± 0.3	13.3	0.80	10.1	394	276	7.65	
	11.09.2003.	1.1 ± 0.2	12.4	0.74	10.0	393	275	7.75	
	18.11.2003.	1.3 ± 0.2	12.0	0.72	9.9	397	279	7.95	
	28.01.2004.	1.4 ± 0.2	12.2	0.73	9.6	392	276	7.95	
Jakuba	19.01.2003.	7.3 ± 0.9	4.6	0.28	6.6	292			gabbro
	19.03.2003.	8.0 ± 1.1	3.8	0.23	5.4	276	193	6.50	
	25.05.2003.	7.8 ± 1.2	5.7	0.34	7.1	275	193	6.30	
	22.07.2003.	7.2 ± 0.9	1.3	0.08	9.8	272	190	6.38	
	07.09.2003.	6.7 ± 0.5	0.7	0.04	10.6	287	201	6.32	
	23.11.2003.	7.1 ± 0.5	0.4	0.02	8.1	288	201	6.35	
	06.02.2004.	9.3 ± 0.8	1.5	0.09	6.5	277	194	6.55	
Lustiga	25.05.2003.	7.0 ± 1.0	4.2	0.25	8.7	293	205	6.05	amphibolite
	16.07.2003.	10.5 ± 1.2	2.3	0.14	10.8	304	213	5.95	
	11.09.2003.	8.6 ± 0.6	0.7	0.04	12.4	293	205	5.95	
	18.11.2003.	7.8 ± 0.5	0.3	0.02	8.0	263	184	6.25	
	28.01.2004.	7.3 ± 0.5	0.2	0.01	3.6	276	193	6.75	
Joanny	22.07.2003.	8.1 ± 1.0	0.6	0.04	13.8	259		6.47	
	07.09.2003.	6.5 ± 0.5	0.1	0.01	13.7	264	185	6.49	

Jasne	19.01.2003.	149 ± 9	66	3.96	8.0	208			granite
	19.03.2003.	154 ± 10	80	4.80	7.4	187	131	6.36	
	25.05.2003.	127 ± 9	74	4.43	7.4	192	135	5.95	
	22.07.2003.	229 ± 14	1.1	0.06	8.4	210	147	6.24	
	07.09.2003.	209 ± 6	1.1	0.06	9.3	212	150	6.32	
	23.11.2003.	166 ± 6	3.6	0.21	7.5	215	154	6.25	
	06.02.2004.	155 ± 5	3.0	0.18	6.0	277	194	6.55	
Korzenne	06.08.2003.	101 ± 7	1.7	0.10	11.4	210	147		
	07.09.2003.	70 ± 3	0.5	0.03	11.5	220		6.60	
	23.11.2003.	76 ± 4	1.0	0.06	8.3	224	157	6.25	
	06.02.2004.	164 ± 5	14.7	0.88	7.2	195	137	6.35	

Tab. 2. **Extreme and mean values of ^{222}Rn concentrations recorded in the spring waters of Ślęża Massif flowing out of different types of crystalline reservoir rocks.**

SPRING	RESERVOIR ROCK	RADON CONCENTRATION (^{222}Rn) [Bq/dm^3]		
		minimum	mean	maximum
Życia	serpentinite	1,1	1,2	1,4
Jakuba	gabbro	6,7	7,6	9,3
Joanny	amphibolite	6,5	7,3	8,1
Lustiga	amphibolite	7,0	8,2	10,5
Jasne	granite	127	170	229
Korzenne	granite	70	103	164

METHODS FOR ASSESSMENT OF THE OCCUPATIONAL EXPOSURE AT WORKING PLACES OF DIFFERENT TENORM INDUSTRIAL BRANCHES

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INTRODUCTION

Within the TENORMHARM project* one task concerns the assessment of the radiation dose to workers of different TENORM industries which are of some relevance within the participating EU and candidate countries.
This assessment is based upon information and data collected at the beginning of the project and, if existing, on national regulations and compared to EU standards.

The most relevant industries of each participating country where TENORM occur were reported by contractors. Each participant selected one branch where an occupational exposure of more than 1 mSv/yr could be expected. Subsequently, the calculation of the radiation dose was carried out independently by each participating country. The results of the dose calculation obtained by each contractor for the selected exposure scenario was than compared with the same or a similar scenario described in Radiation Protection 107 [1].

METHODOLOGY

Selection of industries and working places

The following working places were selected for the assessment of occupational exposure by each participating country:

GRS, Germany	Oil & gas industry: - storage of tubes and drilling equipment - handling with separated scales - removal of scales from tubes - cutting of tubes
NRI, Czech Republic	Titanium dioxide pigment industry: - Ilmenite feedstock - Material in vats - Radium bearing scales
NRIRR, Hungary and ZVD, Slovenia	Coal fired power plant: - ash and slag depository
ICPMRR, Romania	Bauxite processing: - red sludge depository
UGENT, Belgium	Phosphate fertilizer production: - phosphate ore stockpile - waste dumps
UESSEN, Germany and GIG, Poland	Coal mining: - sediments from pit water discharge

Exposure pathways and work conditions

According to the specific features of the above mentioned working places in most cases the following exposure pathways were considered

- external exposure by γ-radiation
- Inhalation of dust
- Inhalation of Radon 222 and progenies

In case of coal mining in Poland and titanium pigment industry in Czech Republic also the direct ingestion was taken into account. In addition, NRI included the exposure by skin contamination because they used the same approach as described in [1].

The considered scenarios are based on realistic work conditions, as appropriate. That means, all measures to avoid or reduce the occupational exposure at each working place were taken into account, e.g. installation of dust suppression systems or air filters.

Dose calculation procedure

For the dose calculation procedure in any participating countries legal frame condition or at least recommendations exist.

In Germany, the dose calculation procedure is described in two regulations on the prediction of dose resulting from uranium mining and milling activities [2, 3]. Nevertheless, some changes of the described dose calculation procedures are necessary in case on hand. That concerns the consideration of nuclides of the Thorium decay chain which are occurring in some TENORM and non equilibrium conditions within and between the natural decay chains, especially in oil & gas industry.

In Czech Republic and Romania no regulation on dose calculation procedures exist for TENORM industries. While NRI applied the calculation procedure according to [1] ICPMRR developed a special procedure for the calculation of dose to man staying on or around a dry red sludge pond.

The Hungarian approach is based on measured values of γ-dose rate and Rn 222-concentration in air (calculated from Rn-exhalation). ZVD (Slovenia) used for dose calculation measured values of γ-dose rate, Rn 222-concentration in air, radionuclides in aerosols and fallout.

The dose calculation applied by GIG is based on the new Polish Atomic Act which came in force on January 2002. According to this regulation, the assessment of dose related to natural radiation shall be carried out in underground mines by means of dosimetric measurements in work environment.

In principle, the following procedure for the calculation of the effective annual dose (D_{tot}) was applied:

- external exposure due to gamma radiation:

$D \; = H \; . f \; . t_{exp}$ (Eq. 1)

H = photon-equivalent dose rate (-DR) [nSv/y]
f = conversion factor from DR to effective dose (0.6 for adults) [-]
t_{exp} = annual exposure [h]

- inhalation of radon and radon progenies:

$D_{Rn} = k(Rn)_A . F . C_{Rn} . t_{exp}$ (Eq. 2)

C_{Rn} = Rn concentration [Bq/m^3]
F = equilibrium factor (0.4)
$k(Rn)_A$ = coefficient pertaining to the dose-convention following ICRP 65 (7.9 E - 6 for workers) [$mSv/Bq . h . m^3$]

- inhalation of contaminated dust:

$D_{LLA} = t_{exp} . V . \sum g_{inh,r} . C_r$ (Eq. 3)

C_r = ambient air activity concentration of nuclide r [Bq/m^3]
V = breathing rate (1.2 m^3/h for workers) [m^3/h]
$g_{inh,r}$ = inhalation dose factor for nuclide r [Sv/Bq]

- direct ingestion of contaminated soil or dust:

$D_{ING} = t_{exp} . U_s . \sum g_{ing,r} . C_{S,r}$ (Eq. 4)

U_s = soil ingestion rate [kg/h]
$C_{S,r}$ = specific actoivity of nuclide r in fine grained fraction of soil [Bq/kg]
$g_{ing,r}$ = ingestion dose factor for the nuclide r [Sv/Bq]

In most cases the direct ingestion of contaminated particles can be neglected if following the principles of radiation and work protection.

The total annual dose results from summing up the dose of each exposure pathway.

COMPARISON OF EXPOSURE SCENARIOS USED BY CONTRACTORS TO SCENARIOS DESRIBED IN RADIATION PROTECTION 107

Applied scenarios defined in RP 107

The report Radiation Protection 107 [1] established reference levels for regulatory control of workplaces where materials are processed which contain enhanced levels of naturally occurring radionuclides.

The exposure pathways according to [1] are the same as described above. In addition, the skin contamination is considered.

The reference levels in [1] which are corresponding to specified dose levels were derived from “normal assumptions” and “unlikely assumptions” defined for two different exposure scenarios of each exposure pathway. In contrast, the dose calculations carried out by the contractors of the TENORMHARM project are mostly based upon measurements of irradiation and radionuclide concentration at a working place or an other location of interest. As far as possible the following scenarios defined in [1] are taken into account for comparison:

1. Exposure from stockpiles

   This scenario presents the exposure of a worker to large piles of material in a warehouse

2. Exposure from scales and residues

   This scenario considers the exposure of workers to chemical or physically concentrated radionuclides, where the two basic assumptions are met:

   - volatilisation of Po (and sometimes Pb) in high temperature furnaces, and
   - enrichment of radium in pipe scales in certain oil and gas fields

3. Exposure from process vessels and pipes,
   where only the external irradiation from a shielded source may lead to an exposure of workers.

Deviating from these scenarios the national reports include exposure situations at outdoor working places.

Because RP 107 is directed towards establishing reference levels for regulatory control of workplaces the dose calculation procedures are sometimes different from that applied by contractors. Therefore the calculation of the dose per pathway in [1] is based on the ratio between the annual effective dose [Sv/yr] and specific activity of an radionuclide [Bq/g]. Subsequently the dose coefficient is expressed as Sv/hr per Bq/g, instead of the dose per activity unit [Sv/Bq]. The dose calculation for skin contamination is based on the ratio between dose rate [Sv/hr] and surface activity [Bq/cm^2].

Data and assumptions used for comparison

According to [1] a classification of the workplace will be carried out using the reference levels given in Table 7b in [1] for “normal assumptions” corresponding to $\leq$ 1 mSv/yr and “unlikely assuptions” corresponding to $\leq$ 6 mSv/yr. Afterwards, the measured individual nuclide concentrations are compared with the reference levels for a particular reference point – in that case the reference point of 1 mSv/yr for “normal assumptions” – given by the formula

$$A_i = \sum_{n=1}^{N} \frac{\text{conc}_n}{\text{reflevel}\ {}^{1}\text{n}}$$

Only if $A_i \leq 1$ does the material contain concentrations below those corresponding to the mentioned reference point. The reference levels correspond to the dose of

1 mSv/yr if the material specific scenarios and parameters are used which are described in Chapter C4 of [1]. That means, if a parameter used by a contractor for dose calculation do not meet its corresponding value of [1] corrections are necessary. Differences between the exposure time can be eliminated by dividing the applied time by the time given in [1] for the concerning exposure pathway for “normal assumptions”.

The comparison of external exposure is more complicated because in [1] the ratio between dose and specific activity (Sv/h per Bq/g) is calculated for a distance of 1.00 m from the source. For some scenarios described in the national reports other distances to the source are used. The relationship between the γ-dose rate (nSv/h) and different distances to the source is given in the German national report [5].

If a reported scenario have no counterpart in [1] the applied dose calculation procedure will be compared with the methods of calculating dose according to section 3.5 in RP 107 using the same exposure time for both calculations.

RESULTS AND DISCUSSION

Table 1 contains an overview of the results of the comparison for selected scenarios and work places described in [4]. As Table 1 illustrates the dose calculated by the contractors is sometimes deviating from the calculation according to [1]. The main reasons for these deviations are summarized in Table 2.

Table 1: Comparison of the results of dose calculation between contractors and RP 107

Exposure pathway	**effective dose [mSv/yr]**	
	reported by contractors	**according to RP 107**
1. Scales in pipes (at drilling platform), GRS		
External exposure (direct contact with pipes)	Ra 226 = 200 Bq/g Ra 228 = 68 Bq/g Th 228 = 80 Bq/g → **1.20 mSv/yr** with T_{EXP} = 400 h/yr	Ext. dose coeff. on Tab. C1 ; (scales in pipes) x 3.33 (direct contact with pipes) → **20.88 mSv/yr** with T_{EXP} = 400 h/yr
2. Removal of scales (by sandblasting), GRS		
External exposure	Ra 226 = 200 Bq/g Ra 228 = 68 Bq/g Th 228 = 80 Bq/g → **0.51 mSv/yr** , with T_{EXP1}, T_{EXP2}, T_{EXP3} as reported in [4]	Ext. dose coeff. on Tab. C1 ; (scales in pipes) x 3.33 (direct contact) and x 0.17 (5.00 m) → **0.14 mSv/yr** with T_{EXP1}, T_{EXP2}, T_{EXP3} adapted
Inhalation of dust	Pb 210 = 0.45 Bq/m^3 Po 210 = 0.45 Bq/m^3 Ra 226 = 1.80 Bq/m^3 Ra 228 = 0.61 Bq/m^3 Th 228 = 0.72 Bq/m^3 → **18.4 mSv/yr,** with T_{EXP} = 500 h/yr	Inhalation dose coefficient on Tab. D9; AMAD = 5 m → **27.8 mSv/yr**
3. Disposal of ash and slag (from coal fired power plant), ZVD		
External exposure	Ra 226 = 0.250 Bq/g Ra 228 = 0.030 Bq/g Th 228 = 0.035 Bq/g → **1.2 x 10^{-3} mSv/yr**	External dose coefficients on Tab. C1 ; (pyrochlore feedstock) → **0.047 mSv/yr**
Radon inhalation	Rn 222 conc. = 50 Bq/m^3 → **0.16 mSv/yr**	Rn dose coeff. on section F3.3 → **0.11 mSv/yr**
Inhalation of dust	Ra 226 = 0.001 Bq/m^3 Pb 210 = 0.06 Bq/m^3 Po 210 = 0.06 Bq/m^3 → **6.2 x 10-4 mSv/yr**	Inhalation dose coefficient on Tab. D9; AMAD = 5 m → **0.15 mSv/yr**
4. Disposal of red sludge, ICPMRR		
External exposure	→ **0.27 mSv/yr** (including background)	Comparable to “Exposure from stockpiles”.
Radon inhalation	0.1 m above ground: Rn 222 conc. = 248 Bq/m^3 → **0.56 mSv/yr** Rn 220 conc. = 6,270 Bq/m^3 → **4.70 mSv/yr**	Assumption: Rn-concentration 1.0 m above ground is 1/10 of 0.1 m value → **0.084 mSv/yr** (Rn 222) → **0.71 mSv/yr** (Rn 220)
Inhalation of dust	U_{nat} = 0.0018 Bq/m^3 Th_{nat} = 0.0025 Bq/m^3 → **0.112 mSv/yr**	Inhalation dose coefficient od Tab. D9; AMAD = 5 m → **0.088 mSv/yr**
5. Flood plain soils affected by pit water discharge from coal mines, UESSEN		

External exposure	exposure time: 200 h/yr → **0.72 mSv/yr**	“Exposure from stockpiles” Ext. dose coeff. on Tab. C1 ; → **0.11 mSv/yr**

Table 2: Reasons for deviation in dose calculation between contractors and RP 107

Scenario/ exposure pathway	Reasons for deviation
1. Scales in pipes	
External exposure	The use of external dose coefficients of RP 107 (Tab. C1) lead to a 10fold higher dose. These theoretical derived dose coefficients do not consider the real conditions sufficiently, e.g. the self absorption of -radiation by $BaSO_4$ and its non-linear relationship to the thickness of scales or the consideration of a pipe as a shielded linear source.
2. Removal of scales	
External exposure	The smaller deviation compared to “scales in pipes” results from better fitting of theoretical assumptions to natural conditions for unshielded volumetric sources.
Inhalation of dust	A significantly higher inhalation dose coefficient is used in RP 107
3. Disposal of ash and slag	
External exposure	Possibly the use of the external dose coefficients (Tab. C1) given for pyrochlore feedstock.
Radon inhalation	No significant deviation.
Inhalation of dust	Possibly significant differences in dose coefficients.
4. Disposal of red sludge	
External exposure	s. Table 1
Radon inhalation	Deviation due to the use of radon concentration measured 0.10 m above ground by Romanian contractor
Inhalation of dust	No significant deviation.
5. Flood plain soils affected by pit water discharge from coal mines	
External exposure	The smaller deviation compared to “scales in pipes” results from better fitting of theoretical assumptions to natural conditions for unshielded volumetric sources. Furthermore the use of the external dose coefficients (Tab. C1) given for radium sludge removal could influence the result.

The applicability of reference levels for regulatory control of workplaces given in [1] seems to be limited because the considered scenarios used for deriving “reference levels” to not reflect sufficiently the recent work conditions. Moreover, any scenarios described by the contractors have no applicable counterparts in [1].

Except for the Czech contractor no party calculated the dose via ingestion of dust and by contamination of skin. According to the modern work conditions and the requirements of measures to prevent an ingestion of contaminated dust this exposure pathway can be neglected in most cases. The same concerns the contamination of skin.

In contrast to RP 107 the TENORMHARM contractors excluded K 40 from the project work. This is an unjustified approach because the dose resulting from K 40 is unavoidable and the ratio between stable potassium and K 40 remains constant all over the world.

The Table C1 of [1] containing external dose coefficients for different industries and materials is highly complicated and its practical application is limited. In practice the use of results from site-specific γ-dose rate measurements is much better suited for external dose calculations because the theoretical approaches in [1] do not reflect the natural conditions sufficiently. Furthermore, these data are not really to reconstruct. The external dose coefficients in Table C1 are given for all long lived naturally occurring radionuclides for a lot of different materials. The most of the listed radionuclides can be neglected for external dose estimation. Only some decay products of Ra 226 and Ra 228/Th 228 (and K 40) contribute to the external dose by γ-radiation.

That is the same for reference levels in Table 7a – 7d. In case of such raw materials which are remaining the equilibrium of the natural decay chains always the nuclide with the highest contribution to the dose is defining the activity level of interest and, the ratio between U 238+ and U 235+ is unchanged. Also for non equilibrium conditions this scheme is questionable. If we consider for example the reference levels of Ra 228 and Th 228 in radium scales where the value of Th 228 is one order of magnitude lower than for Ra 228. If Ra 228 is acting as starting point of the segment of the Thorium decay chain the specific activity of Th 228 will reach a (theoretical) 1.46 times higher activity as Ra 228 after a certain time and, in parallel decaying with the half life of Ra 228.

SUMMARY AND CONCLUSIONS

1. In majority of investigated cases of TENORM at work places the occupational exposure can not be reliable assessed automatically by applying standardised factors. For this purpose only possible pathways shall be listed and general rules of assessment shall be prepared.
2. In each case the assessment shall be done basing on the direct measurement of particular risk factors. Only in this way all influencing features can be considered (certain work condition, geometry, attenuation, individual protection, respiratory means etc.).
3. In principle, only the external exposure, the inhalation of Radon and dust contribute to the total occupational exposure. The dose via direct ingestion of particles and skin contamination is avoidable by common radiation protection and hygiene measures.
4. All investigated practices should be additionally assessed by considering their impact to the members of the public.
5. For evaluation the significance of risk occurring in all investigated branches of industry the concepts of clearance, exemption and exclusion should be applied according to RP 122 [6].

REFERENCES

Radiation Protection 107
Establishment of reference levels for regulatory control of workplaces where materials are processed which contain enhanced levels of naturally occurring radionuclides.
European commission, 1997

Commission on Radiological Protection (SSK)
Berechnungsgrundlagen zur Ermittlung der Strahlenexposition infolge bergbaubedingter Umweltradioaktivität (Berechnungsgrundlagen – Bergbau).
Draft, July 1999

Commission on Radiological Protection (SSK)
Berechnungsgrundlagen zur Ermittlung der Strahlenexposition durch Inhalationvon Radon und seinen kurzlebigen Zwerfallsprodukten infolge bergbaubedingter Umweltradioaktivität (Berechnungsgrundlagen – Bergbau: Teil Radon).
Draft, July 1999

Central Mining Institute (GIG) and Gesellschaft fuer Anlagen- und Reaktorsicherheit (GRS) mbH
Radiation risk assessment methods and guidance for ist application.
EU-project TENORMHARM, Comparison and Summary of national reports (Deliverable No 2), April 2003

Gesellschaft fuer Anlagen- und Reaktorsicherheit (GRS) mbH
Radiation risk assessment methods.
EU-project TENORMHARM, Deliverable No 2 of Germany, March 2003

Radiation Protection 122
Practical use of the concepts of clearance and exemption. Part II – Application of the concepts of exemption and clearance to natural radiation sources.
European commission, 2001

PROPOSAL OF THE SWEDISH COMMITTEE ON MANAGEMENT OF NON-NUCLEAR RADIOACTIVE WASTE (IKA) AND THE IMPLICATIONS FOR THE MANAGEMENT AND STORAGE OF TENORM AND NORM WASTE

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ABSTRACT

The Swedish Government Committee on Management of Non-Nuclear Radioactive Waste (IKA) had the commitment to propose regulations regarding NORM waste to be included in the Swedish Radiation Protection Law and the Radiation Protection

Ordinance. The Committee delivered its proposals to the Government by 1st December 2003.

The production, handling and storage of materials classified as TENORM and NORM has earlier not been subject to legal regulations, but is now to be included in the Radiation Protection Law and Ordinance. Waste that will be subject to the new regulations are for example, ashes containing NORM and ashes of biofuel containing cesium-137 from the Chernobyl accident, uranium-rich skarn from mining of iron ores (even if the mine was abandoned many years ago), gypsum waste from phosphate production, alum shale burnt to extract oil (there exist more than 50 million $m^3$of such material), filters and sludge from water treatment equipment and pipes and pumps contaminated with radium due to precipitation from water.

The Committee proposes that the producer that utilizes raw material containing naturally occurring radioactive substances shall have the full responsibility for future depositing of the waste. The responsibility shall include a fee to a new Government fund to cover the total costs for management and future storage of the waste. This fee is to be paid by the producer of the waste material.

In case the waste consists of material from old use of natural radioactive material with no present owner, e.g. uranium use for colouring ceramics, the fund may in some cases cover the cost. This might also be the case when the disposal costs are unreasonably high for a private person, e.g. for disposal of resins used for treatment of water, which is contaminated with so high concentrations of uranium or radium that it has to be handled as radioactive waste. Radioactive waste from old abandoned mines, e.g. uranium mineralised waste rock at old iron mines or alum shale excavations where no present owner has the responsibility for the waste are proposed to be regarded as contaminated sites and thus entitled to the same Government funds that are used for restoring land contaminated by chemical substances.

The Swedish Government Committee on Management of Non-Nuclear Radioactive Waste (IKA) also has given proposals for future storage of other kinds of non-nuclear material, for example highly radioactive sources used in industry, radioactive hospital waste and smoke detectors.

INTRODUCTION

The following text is mainly based on a summary of the report SOU 2003:122 from the Swedish Government Committee on Management of Non-Nuclear Radioactive Waste (IKA) submitted to the Swedish Government in December 2003 [1]. In our text we have concentrated on the Committee's proposals for TENORM and NORM. At present most of TENORM and NORM materials are not subject to regulations as their content of radioactive elements are lower than the Swedish exemption levels. As an example, the exemption level for uranium-238 in equilibrium with its decay nuclides is 10 kBq/kg. The IKA-investigation has also given proposals for future storage of other kinds of non-nuclear material, for example highly radioactive sources used in industry, radioactive hospital waste and smoke detectors. An extensive summary of the investigation is given in Safe Management of Non-nuclear Radioactive Waste. Summary of the Swedish IKA-investigation SOU 2003:122. (Copyright ÆÉ by WM Symposia, Inc. All Rights Reserved. Reprinted with permission.) For the full summary see:
www.sou-gov.se/ikautredningen/PDF/Summary_SOU-2003-122.pdf

Directives

The Swedish Government on 23rd May 2002 decided to set up a non-standing committee on Non-nuclear Radioactive Waste. According to the directives of the Committee, the objective was to analyze and propose a national system for the handling and final disposal of non-nuclear radioactive waste. The system must involve a well functioning solution with regard to organization, the environment, finance and legislation. The Committee adopted the name the IKA Committee (IKA – a Swedish abbreviation for non-nuclear radioactive waste i.e. radioactive waste unrelated to nuclear technology). Representatives from the Ministry of the Environment, the Swedish National Environmental Protection Authority, the Swedish Radiation Protection Authority (SSI), the Swedish Nuclear Power Inspectorate, the Swedish Rescue Services Agency assisted the committee. This group also included representatives from the Confederation of Swedish Enterprise and the Swedish Nuclear Fuel and Waste Management Company (SKB), owned by the nuclear power industry. The SKB now has the task of taking care of Sweden's spent nuclear fuel and the radioactive waste from the nuclear industry.

Comprehensive aims and principal starting points

A natural starting point is the environmental objective of a Safe Radiation Environment (*Säker strålmiljö*) (bill 2000/01:130 Swedish environmental aims – objectives and strategy measures) [2] that, among other things, states that:

- By 2010, the content in the environment of radioactive substances that are released by every enterprise must be so low that public health and biological diversity are protected. The additional individual dosage to the public must fall below 0.01 mSv/person/year from each separate enterprise.

To this, the government added a clarification that:

- Radiation doses are to be kept within bounds as Low As Reasonably Achievable (ALARA).
- The highest total annual effective radiation dose, that a member of the public may be exposed to from an enterprise involving radiation, must not exceed 1 millisievert (mSv) per person during a one-year period.

In many cases, these aims and principals establish the absolute dose limits for people and the environment. The IAEA "Joint convention on the safety of spent fuel management and on the safety of radioactive waste management" establishes the fundamental principal that the handling of radioactive waste must not be put onto the shoulders of future generations.

When it comes to a system for the handling and final disposal of non-nuclear radioactive waste, the principal starting points for being able to meet the above stated aims for overall protection against radiation, as well as the aims and starting points for an environmentally adapted waste handling, can be summarized as follows:

1. With regard to *waste*, the following should apply:
   - All radioactive waste, except for that classified as cleared, should be collected and taken care of ("100 % requirement").
   - The amount of waste should be minimized and any danger due to waste is to be successively reduced.
   - The ALARA principel for radiation doses must be put into practice.
   - The handling of non-nuclear radioactive waste must fulfil the demands for protection against radiation, in accordance with the overall radiation protection aim and norms for
   - a. The workers handling the waste

- b. the public and the environment
- c. minimizing the discharges and risks for accidents
- Properties other than the ionizing radiation of waste must be taken into consideration, e.g. biological and chemical properties.

2. The *national waste system* should fulfil the following demands:
   - The waste system must be organizationally, environmentally, financially and legally well functioning
   - A defined producer responsibility must apply, as far as possible
   - The handling of radioactive waste must not impose undue burdens on future generations.

Product Waste, Industrial Waste and Other Waste

The Committee divides non-nuclear radioactive waste into three main categories:
Product waste, which includes household products as well as products used in research, industry and hospitals etc. For this category it is easy to identify a producer who imports or manufactures the product and puts it on the Swedish market. Such activities need a license from the Swedish Radiation Protection Authority (SSI) according to the Swedish Radiation Protection Ordinance [3].
In this category are included both products that require authorization for handling in all aspects, e.g. strong sealed radiation sources, and mass-consumption items, such as single-unit smoke detectors (with a battery), where only the manufacturer/importer is required to have authorization for handling.
Industrial waste. Radioactive substances appear naturally in nature. These substances can become concentrated in certain industrial operations that handle large amounts of naturally occurring substances. This type of waste includes TENORM, NORM and biofuel ashes from combustion plants. Most of these processes are licensed anyway under the Environmental Code and funding for the

management of the radioactive waste emanating from such practices can be settled in the licensing procedure along with specific conditions on the generation and handling of the waste.

Other Waste. This concerns waste that is neither Product Waste nor Industrial Waste. It can include certain production waste, older waste or abandoned waste without any legally responsible owner. It also includes waste with no known owner, e.g. orphan sources and radioactive waste discovered in scrap metal. *Other Waste* is a minor contributor of waste compared to the other two main groups and the necessary surplus of the funding system may well cover the costs also for the management of this waste.

PROPOSALS FROM THE COMMITTEE

Producer Responsibility

The Committee proposes that:

- All producers of products, with radioactive substances as components or products in the form ofradiation sources, must be imposed with a producer responsibility for the waste that arises when the product or the radioactive component is discarded or scrapped (Product Waste). By producer, is meant the one that produces, imports into the country or releases products on the market that give rise to radioactive waste. This responsibility must include an obligation for taking back the products after completion of use and for being in charge of the final handling of the waste.
- Producer responsibility should include a fee that would go to a special state fund for meeting the total costs of handling any arising radioactive waste, including final disposal if it is dealt with in Sweden.

- When it comes to waste to be taken back by a supplier for final disposal in the country of origin, a bank guarantee or the equivalent should be insisted on.
- The fee must meet a reasonable share of the total costs of the historic waste for which no financial producer responsibility was previously in force.
- A State fund is established for collecting and administering the fees that producers pay for the handling of non-nuclear radioactive waste (The IKA Fund), together with making payments under the authorization of the Swedish Radiation Protection Authority (SSI).
- The Fund should be tied in with the existing Nuclear Waste Fund and share the same administrative body.
- SSI should be given a wider role when it comes to producer responsibility
- for checking authorization and keeping a register of producers
- for establishing and debiting fees
- for receiving compensation demands and approving disbursements
- for issuing instructions concerning handling and financing of non-nuclear radioactive waste
- for checking and monitoring the waste handling system.
- A special advisory committee with representatives from the side of the producers and authorities should be attached to SSI for following up and scrutinizing SSI activities within this area. The committee should also be able to make decisions on recommendations concerning the activities.
- The new system of producer responsibility for non-nuclear radioactive waste should come into effect on13th August 2005, concurrently with the new regulations that intend to implement the EU Directive 2002/96/EG [4], concerning waste from electrical or electronic products.

Industrial Waste

The Committee proposes that:

- Radioactive Industrial Waste, i.e. radioactive waste that arises through enrichment of naturally occurring radioactivity or through the handling of biomass containing fall-out from nuclear weaponry tests or nuclear technology accidents, e.g. combustion of bio fuels, must be handled according to the Swedish Environmental Code [5] regulations, regarding ecologically harmful activities.
- Operations that can be thought of as giving rise to radioactive Industrial Waste should, in the first place, be tested for authorization, according to the Swedish Environmental Code, and this must be preceded by a description of the environmental consequences regarding radiation risks and the genesis of Industrial Waste.
- Operations that give rise to Industrial Waste but which have not been tested for authorization, according to the Environmental Code, must be regulated through the application of the Radiation Protection Legislation.
- It must be possible for permits for ecologically harmful operations to include conditions about preventive measures that aim at avoiding or restricting radioactive waste arising, as well as conditions for how waste is to be managed and taken care of or to include a delegating to the supervisory authority to issue further regulations about the management of the waste.
- In cases where the Environmental Court or a County Administrative Board issues conditions concerning the taking care of radioactive Industrial Waste that involves demands for financial security, an enterprising party should pay a fee to the IKA Fund to guarantee that the waste can be taken care of correctly on the discontinuation of the operations. This is to be regulated in the legislation concerning the setting up of the IKA Fund.
- The radiation protection legislation be altered, so that Industrial Waste is covered by the provisions of the legislation, concerning responsibility for

radioactive waste through the Radiation Protection Ordinance being made applicable to Industrial Waste.

- SSI should
  - where applicable, issue general instructions for the management and final disposal of certain Industrial Waste, with the support of the Radiation Protection Act [6], in accordance with the above mentioned amendments.
  - be granted the right to be able to request a reappraisal of operations that give rise to radio-active Industrial Waste, according to the Environmental Code, and to be identified as the supervisory authority in the Ordinance for supervision [7].
  - be given the mission of informing about problems with radioactive Industrial Waste in the respective trade journals and to publish general advice on the management of such waste.
  - confer with the Swedish National Environmental Protection Authority for being responsible for the supervisory and regulatory committee. SSI ought to be included in this committee.

Other Waste

The Committee proposes that:

- Those, liable for payment to the IKA Fund, deposit a proportionate contribution to the Fund, in order to meet the costs for dealing with any other waste, where it is not possible to establish a legally responsible party for the waste.
- Within their present inventory program and yearly suggestions concerning measures to decontaminate contaminated land and deal with hazardous waste in old industrial plants, the County Administrative Boards should be given the mission to include radioactive waste and radioactive contaminated land. SSI should be given the mission to assist the County Administrative Boards and the Swedish National Environmental Protection Authority with information and expert knowledge in this work. The appropriation for decontaminating and dealing with hazardous waste should, where appropriate, also be available for measures to decontaminate the radioactive waste.
- Those operating activities with radiation, which give rise to contaminated matter or induced radiation, must be able to be charged with paying the fee for dealing with the waste to the IKA Fund.

Clearance

The Committee proposes that:

- SSI be given the opportunity to make decisions about general exceptions to the Radiation Protection Act [6], when this is well founded, from the point of view of radiation protection and when it concerns the demands for an effective management of non-nuclear radioactive waste; a so called *clearance*.
- Amendments are made to the Radiation Protection Ordinance [3] to achieve this goal.

Final Disposal and the Role of Swedish Nuclear Fuel and Waste Management Company (SKB) and Studsvik in the Waste System

The Committee's proposal for final disposal:

At the earliest possible opportunity, the State should commence negotiations with Swedish Nuclear Fuel and Waste Management Company (SKB), regarding a general agreement for the final disposal of non-nuclear radioactive waste, based on the grounds that the Committee discussed with SKB during the investigation. These imply, among other things, that SKB undertakes the final disposal of all non-nuclear radioactive waste that requires such final repositories as in any of its existing or future plants and will do this for, principally, cost price. Furthermore they imply that SKB must be able to receive compensation also for actions taken for the adaptation of the storages and for the reappraisal of the licensing conditions for the repositories when necessary.

The Committee's assessment of Studsvik AB (Ltd.)

In the 1950ties the main part of Swedish nuclear research was localised to Studsvik, on the east coast 100 km south of Stockholm. There two research rectors were built and a waste handling system and an intermediate repository for low and medium radioactive waste. From the beginning the enterprise at Studsvik was state owned but it is now privatised. As Studsvik AB is the only Swedish enterprise that handles non-nuclear waste the company has a monopoly position on the market for services. This is now a problem as Studsvik AB has no obligation for taking care of radioactive waste and the cost for future storage of long-lived radioactive waste is not known. Thus Studsvik can refuse to handle and dispose of radioactive waste if the cost for storage is not covered or that it contains long lived nuclides, e.g. radium or thorium. Also the costs for handling and storage are so high that private persons or small enterprises can't bear them.

However these problems will substantially decrease, if the Committee's proposals for a national system for non-nuclear radioactive waste are realized. The grounds for Studsvik AB, and any other possible players on the market, for not handling certain kinds of radioactive waste, disappear in part or completely. The Committee therefore concludes that there is presently no need for any duty, regulated by law, to take care of non-nuclear radioactive waste. Nevertheless, the Government ought to closely follow the development of this issue.

DELIBERATIONS

Clearance

Today, SSI is unable to issue regulations on clearance (i.e. exceptions to the entire Radiation Protection Act application), except that it may decide about clearance when it comes to individual cases.

However, there are good possibilities for introducing a more operative clearance system in Sweden – without waiving the basic radioactive protection demands or obstructing the environmental goal for a secure radioactive milieu from being reached – that stands in agreement with the EU regulatory framework. Further development work in SSI is needed, however, before an operative system for clearance can begin, which will meet the highest demands placed on radiation security. It is taken for granted that a change is made to the Radiation Protection Ordinance [3]that will permit general decisions about clearance from the Radiation Protection Act's application [6].

SSI has pointed out a list of problems with the current management of the radioactive waste. One point concerns the case when an operator of an enterprise goes bankrupt or closes down operations. Waste from radioactive sources may then lack a legally responsible person, who can cover the costs for the management and possible final disposal of the waste. The same thing concerns orphan radiation sources that occur in nature or at waste service sites. A producer responsibility, that lays the responsibility for the waste management on the producer and not on the owner, has a great potential for being able to substantially reduce the number of cases, where an owner could consider disposing of a hazardous radiation source illegally or in an inappropriate manner. The hazardousness of the radioactive waste and the need for being able to take care of all waste provides motivation for a producer responsibility. A suitably formulated producer responsibility makes it also possible to successively reduce the amounts of waste and diminish the hazardousness of the waste. Generally, there is a direct relationship between the amount of waste that a radioactive product gives rise to and the costs for dealing with the waste. Reduced activity in the product simplifies the management in all aspects, when it comes to taking care of the waste. Reduced activity and short-lived isotopes diminish the demands on final disposal and, therefore, make the waste management cheaper.

Even when designing a product, producers have greater opportunities of taking these possibilities into account for making the products cheaper to deal with.

In the Committee’s opinion, there is, therefore, motivation to develop a system of producer responsibility for radioactive products. Moreover, such a producer responsibility has to be added to the existing Radiation Protection Act regulatory framework.

A producer responsibility for radioactive Product Waste should partly include an obligation for the producer to be responsible for the collecting, management and final disposal of radioactive waste, and partly a liability to leave financial guarantees for the managing and final disposal of the waste. Producer responsibility should also include historic waste, like orphan radiation sources. In the Committee’s opinion, the producer responsibility model is the system that best meets the demands made on non-nuclear radioactive waste, with regard to Product Waste. This also has the advantage of leaving considerable room for the market to formulate the systems that can provide for collecting, managing and final disposal, if necessary, in a cost effective manner.

Demands for Financial Solutions

A system with financial guarantees must be created for dealing with radioactive waste, so that needed resources can always be guaranteed. Due to the hazardousness of the waste, there is motivation for not allowing radioactive substances to become orphan or to be illegally utilized for anti-social purposes. Even if companies go bankrupt or change the direction of their operations, the necessary resources must exist for taking care of the radioactive waste.

When it comes to non-nuclear radioactive waste, the demands have to be high. A financial system for non-nuclear radioactive waste ought to meet the following demands:

- Have the potential to result in a 100% safekeeping
- Secure financing over a long period
- Provide high and secure yields on established resources
- Allow fees or appropriations that lead to reduced amounts of waste and diminished hazardousness in the waste
- Must function well
- Organizationally
- Environmentally
- Financially and
- Legally

The demands will be especially clear, if one considers the case that, in most instances, radioactive waste must be stored, sealed in special rock shelters for many centuries. Suitably sealed storages do not presently exist and will not become a reality for another 30 years or so. The financial resources have to also be secured for long periods. The delay is so long that many companies might have left the market for various reasons, when the costs for final disposal arise.

Today, there exist four state funds for waste. They are the Nuclear Waste Fund, the Studsvik Fund, the Battery Fund and the Car-Wrecking Fund.

The Nuclear Waste Fund. The Nuclear Waste Fund is a state fund system, created in 1981 to ensure financing of radioactive waste from nuclear power stations. The financing is regulated by legislation (1992:1537) concerning the financing of future expenditure for spent nuclear fuel. The fund has a book value of SEK 29.4bn (approx. €3.2bn) and a market value of SEK 31.3bn (approx. €3.4bn).

The Studsvik Fund. Fund for financing existing waste from, among others, the closed combined power and heating nuclear plant in Ågesta, and the closed research reactor, R1, in Stockholm, and waste from the research reactors at Studsvik.

The Battery Fund. The battery Fund is a state funding system to ensure the taking care of environmentally hazardous batteries. The total balance for mercury batteries is SEK 68·4m (approx. €7.4m), for lead batteries SEK 262m (approx. €28.5m) and for nickel cadmium batteries SEK 243m (approx. €26.4m). The total fund balance amounts to SEK 573m (approx. €62.3m).

Other financial solutions. As set out above, there are several alternative solutions for guaranteeing the financing of radioactive waste. Along with the state funds for covering the costs of waste, there are also examples of private solutions. These apply to, for example, electronic waste and, in part, mercury.

The Committee proposes a State Fund. On the basis of the discussion going on regarding the possibilities of meeting the demands placed on the financial mechanism for radioactive waste, a state fund is the Committee’s proposal for guaranteeing resources for managing radioactive Product Waste.

As will be seen from the Committee’s proposal concerning Industrial Waste and Other Waste the proposed state fund solution could also be utilized for Industrial Waste as well as certain Other Wastes. When it comes to the administration of paid resources, the association of the IKA Fund with the Nuclear Waste Fund is the only realistic and efficient alternative.

Waste Resulting from Concentration of Naturally Occurring Radioactivity

Industrial waste

Radioactive substances occur naturally in nature. One example is radium. They can be enriched and concentrated in certain industrial processes, which deal with large amounts of naturally occurring substances. This applies, for example, to water flows in pipes and contaminated oil. Industrial water is filtered in many contexts and these filters can concentrate radioactive substances that occur naturally. This even applies to heat exchangers and municipal drinking-water treatment works. Peat ash and ashes from combustion of bio fuels may contain significant amounts of radioactive substances. Ashes from bio fuels may contain cesium 137.

This waste, usually called NORM (*Naturally Occurring Radioactive Material)* or TENORM *(Technically Enhanced NORM*), has to be introduced into the waste-flow under the same criteria as for other radioactive waste. It occurs, in most of the cases, in activities that do not have activities involving radiation as a primary objective, i.e. that are not in operation with radiation, according to the definition in the Radiation Protection Act [6]. The enriched or concentrated radioactivity is an unwanted by-product, as is other types of waste or pollution from operations. Waste that occurs, in the manner described in enterprises that are not licensed to operate activities involving radiation, is called Industrial Waste.

The Environmental Code and radioactive industrial waste

According to the Environmental Code [5], environmentally hazardous operations are considered to be, among others, the use of land, buildings or installations in such a way that inconvenience may occur to the surroundings through ionizing or non-ionizing radiation, among other things. This makes it possible to assess such operations for authorization that give rise to inconvenience, due to radiation from radioactive waste, as an example. The Code also states that it can be forbidden to release or store solid waste or other solid substances, if this can lead to land, water areas or ground water being polluted without authorization.

Furthermore, according to the Environmental Code [5], all who operate activities must take the protective measures, observe the limitations or practice the precautionary measures necessary for protecting against damage or inconvenience to people's health or the environment. The Environmental Court or a County Administrative Board realizes a permit appraisal for environmentally hazardous operations. According to the Environmental Code, a judgement on a permit, where appropriate, contains decisions about the conditions necessary for the management of waste and recycling and re-utilization if the management, recycling or reutilization can give rise to inconvenience for the external environment. The permit appraisal organ can further commission the supervisory authority to issue detailed conditions for dealing with waste. It is, consequently, fully possible to assess radioactive Industrial Waste for authorization, according to the Environmental Code.

In the Environmental Code, there are regulations concerning Accounts of Environmental Consequences (MKB). These constitute an important component, when assessing Industrial Waste. SSI has to play a proactive role in informing about problems with radioactive Industrial Waste, aimed both at the permit assessing authorities and the supervisory authorities, as to the lines of business involved.

It must be the role of SSI to be able to issue general advice and instructions for Industrial Waste, operative supervision and supervisory guidance in those cases where, according to the Environmental Code, other organs are the supervisory authorities. This could be achieved by adding SSI in *the Ordinance (1998:900) regarding supervision [7], according to the Environmental Code [5]*. This implies that the authority would be included in the supervisory and regulatory council of the Swedish National Environmental Protection Authority.

SSI has suggested to the Committee how the definition of operations involving radiation, in the Radiation Protection Act [6], could be expanded to make it possible to issue general advice and instructions in those cases where Industrial Waste is not appraised, according to the Environmental Code. This would be achieved through an amendment to the Ordinance on supervision according to the Environmental Code.

The Environmental Code applies, parallel with the Radiation Protection Act. Those that operate activities with radiation are also liable, apart from the provisions in the Radiation Protection Act, to observe and put regulations of the Code into practice. If a conflict between the legislation should arise, i.e. a regulation in the Environmental Code should be inconsistent, in relation to some regulation in the Radiation Protection Act, then the provisions in the Radiation Protection Act take precedence over the Environmental Code. According to the Environmental Code, the permit appraisal authority should pay attention to these relationships during the appraisal itself.

Connection to the financing system for product waste

With the aid of the Environmental Code regulations, it is possible to make demands on operators of activities to allocate resources for after-treatment, by taking care of arising waste. The easiest way of achieving this is for the permit appraisal authority, in the permit, to enlighten the operators of the activities that they are liable to pay a fee, according to legislation for the financing of non-nuclear radioactive waste. In this way, the IKA Fund could be a general instrument for the financing of radioactive waste that demands financial guarantees for being taken care of and/or for final disposal, if necessary.

Final Repository Capacity

At present in Sweden an underground repository for low and medium waste (SFR) exists at the Forsmark Nuclear Power Plant. The owner of this repository is SKB. A final underground repository for highly active and long-lived waste (SFL) is to be built within 30 to 40 years. At Studsvik non-nuclear radioactive waste can be temporarily stored. There is a rock shelter for 6,000 m^3 of packaged waste, with a large available capacity. With the information available and with today's know-how, the Committee estimates that this space will probably be sufficient for the whole period of 40 to 50 years until SFL is ready.

SKB and final disposal

Today, SKB has no direct obligation to accept non-nuclear radioactive waste, but SKB has itself expressed its ambition thus: "We take care of Sweden's used nuclear fuel and radioactive waste so that the environment and people's health are protected in the short and long term." As a basis for this, SKB has undertaken to finally dispose all non-nuclear radioactive waste that can be disposed of in a SKB final repository, under certain conditions. According to SKB, the principle would be cost price for final disposal. Resources from the IKA Fund could be requisitioned to cover the increasing general costs for the licensing or re-licensing that could be demanded, so that it will be possible to finally dispose certain substances and material that were not originally included in the planning.

As stated, the matter of final disposal should not be any great problem in the future, from the aspect of capacity. Non-nuclear radioactive waste volumes are significantly less than the volumes of nuclear waste, even if the isotope combination can vary. With the final repository that exists, SFR, and the planned final repository, SFL, it should be possible to finally dispose all non-nuclear radioactive waste within the foreseeable future. Under certain circumstances, a commercially practicable alternative could be to use additional space in the planned rock shelter repository for mercury.

Forms for ensuring that Studsvik accepts radioactive waste

If the Committees proposals are realised, Studsvik no longer needs to absorb risks, when it comes to final disposal. Those responsible for producing waste or other parties can close their own agreements with SKB, if the final disposal part and Studsvik's services can be purchased separately. With that, the Studsvik operations and offered services will be wholly independent and there will be well-defined sections in the waste management chain. The Committee expects that the market, with its prerequisites, will solve the problems for Studsvik in its present situation and the problem of Studsvik's monopoly position will mainly disappear. The new market situation could also open up for market participants, other than Studsvik AB. This means that, even if it is possible to legislate for an injunction for handlers of waste to accept radioactive waste, then this solution should not be used in the situation that is expected to arise.

SURVEYS

Types of Waste and Waste-Flows

Consumer items

Included in this category are smoke detectors and products, which are sold as night-seeing aids, in the form of telescopic sights, bearing compasses and bearing binoculars. A deal of radioactive waste also occurs from consumer items from former times, when it was permitted to use clocks with luminous faces and uranium compounds could be used to give a lustre to colors on ceramics and, sometimes, even on crockery and glass.

NORM – TENORM etc.

This type of waste mainly comes from industrial processes that use large volumes of naturally occurring radioactive substances (NORM*)*. These have, as a rule, been enriched through the processes. A technical term for this is TENORM. Residue waste, such as slag from mining operations, sand filters or the equivalent from water works etc. are, in certain cases, so enriched with natural radioactive substances with long half-life, that the waste must be taken care of in a special manner.

Combustion of bio fuels and peat gives rise to ashes with increased contents of radioactive cesium, predominantly from fallout after the Chernobyl accident. About 100,000 tonnes of bio fuel ash from wood fuel and 30,000 tonnes of peat ash are produced annually.

Depleted uranium is a residue product that remains, when natural uranium is enriched to form nuclear fuel or nuclear weapons. It is only when the depleted uranium has to be taken care of as waste, that it presents a radiation protection problem. By a rough estimate, there are a few dozen tonnes of it in Sweden. The biggest environmental hazard comes from the chemical toxicity of uranium.

Open and sealed radiation sources

Sealed radiation sources in industry are sometimes returned to the supplier when they are scrapped, but it is often the owners, themselves, who are responsible for the waste being taken care of within the country. Non-nuclear radioactive waste from hospitals, research and education often consist of *open* radiation sources, e.g. when the radioactive substance is found in the form of a liquid solution. At a rough estimate, Sweden generates a few dozen kilograms of waste from radioactive chemicals each year, which does not cause any great waste problem. Solid waste from these operations can be protective clothing, glass jars etc. with small amounts of radioactive substances. The suppliers take most of the sealed radiation sources back as a rule, in some kind of exchange system. For practical reasons, the scrapped sources are always sent abroad to the country they came from, in such cases. However, radiation sources from the medical care sector still occur which, after many years'usage, must be sent to Studsvik to be taken care of. Activities in research, hospitals and education are expected to continue at the present rate.

To sum up, it concerns one to two hundred strong to medium strength radiation sources from industry, hospitals, research and education that need to be finally disposed of in Sweden, every year.

Abandoned radiation sources lack known lawful owners, responsible for their scrapping. In today's circumstances, the one who finds such an orphan source, becomes likewise its owner and, with that, according to the Radiation Protection Act [6], is responsible for taking care of it. It is important to build an efficient system for reducing risks from abandoned sources, since these can be the cause of grave consequences with financial damages and acute radiation injuries. The International Atomic Energy Agency (IAEA) in Vienna has also warned against terrorists using orphan radioactive waste to make terror bombs, the so-called *dirty bombs*. In Sweden, abandoned radiation sources are reported to SSI once or twice a year.

EXPECTED OUTCOME

The IKA-Committee's proposals are now handed over to the Government. After remittance the Government final proposal will probably be presented to the Parliament early in the year 2005. It is expected that the new regulations and agreements will be in force later in 2005.

REFERENCES

SOU 2003:122, Radioaktivt avfall i säkra händer, Betänkande från utredningen om radioaktivt avfall från icke kärnteknisk verksamhet (IKA), Statens offentliga utredningar, Stockholm 2003. www.sou-gov.se/ikautredningen/PDF/Summary_SOU-2003-122.pdf

Sweden's environmental objectives no. 6: A safe radiation environment.

Swedish Radiation Protection Ordinance (1988:293).

EG 2002, Council Directive 2002/96/EG of 27 January 2003 on waste electrical and electronic equipment (WEEE), Official Journal L 37/24, 13.2.2003.

Swedish Environmental Code (SFS1998:808).

Swedish Radiation Protection Act (SFS 1988:220).

Ordinance on supervision according to the Environmental Code (SFS 1998:900).

EG 2003, Council Directive 2003/122/Euratom of 22 December 2003 on the control of high-activity sealed radioactive sources and orphan sources (HASS), Official Journal L 346/57, 31.12.2003.

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ASSESSMENT OF THE RADON CONTRIBUTION FROM MINING SITES TO THE GEOGENIC ENVIRONMENT

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Abstract

An issue of NORMs in mining areas is the mean ‘Rn-exposure’ assignable to surface mining residues. Outdoor Rn-decay chain concentrations (at breathing height), compared with elevated indoor levels, are relatively low and they fluctuate widely with time and location. Differentiating a mining contribution of ‘Rn-exposure’ from a geogenic exposure is a challenging metrological task, particularly in the later stages of remediation. The activity concentrations of Rn decay chain members can be determined accurately with good time resolution down to low outdoor concentrations

using (quasi-)continuous on filter concentration measurement. Such measurements showed continuous diurnal concentration cycles ranging from a general minimum concentration to a widely varying maximum for different cycles. Correlation with chain activity ratios and diurnal wind velocity clarifies the buildup of concentrations near the ground during minimal vertical air exchange, above an otherwise generally low concentration over the height of the atmosphere. Ways of assessing Rn exhalation and of the exhalation ratio ^{222}Rn/^{220}Rn are indicated, and these may provide a better measure for assessing possible mining influence on local Rn exposure.

Introduction

Radon concentrations fluctuate widely in time and space, and outdoors at breathing height, apparently of interest to some groups, it is difficult to differentiate relatively small increases in 'average' Rn concentrations which could possibly have resulted from current or past mining activities. At this height above ground diurnal concentration cycles of varying magnitude generally occur due to diurnal cycles of air movement. To assess possible contributions from mining activities, diurnal cycles of different character were investigated to elucidate the processes leading to long-term mean concentrations. Many previous studies with long-term (seasonal) integrated measurements had not yielded mean geogenic Rn concentrations at hoped-for small error margins. An explanation for this has been derived here from diurnal cycle periods of vastly different intensity that have been investigated so far.

The Rn exhalation rate from the ground has a much closer link to possible effects from mining activities than the Rn-concentration in air and a new method of local exhalation assessment is proposed.

Rn measuring instruments

For the measurement of outdoor Rn concentrations down to a few Bq/m^3, a range of instruments is available - from low sensitivity instruments for long term (monthly to annual) integrated measurement, to much higher sensitivity instruments for continuous measurement of concentrations differentiated hourly or shorter. With long-term integrating measurements the individual processes dominating the average Rn concentration over short time periods cannot be unfolded.

In any measuring instrument all members of the sampled decay chain are involved and ought to be considered when accurate evaluation is favoured. Direct gas measuring instruments are generally equally sensitive to ^{222}Rn and ^{220}Rn. With an often very substantial contribution from ^{220}Rn outdoors (even to a height of many metres above ground), not considering ^{220}Rn can lead to respectable errors in the conversion of measurement signals to ^{222}Rn concentration. As shown in table 1, with on filter concentrating-, α–spectrometric instruments outdoor ^{222}Rn-concentration can generally be measured far more accurately than with direct Rn-gas instrumentation, and they are insensitive to ^{220}Rn and ^{216}Po concentrations. On filter concentrating instruments, in addition to providing the ^{222}Rn-concentration, can simultaneously furnish also the potential α-energy concentrations ^{222}Rn- and ^{220}Rn-PAEC, as wells as the ^{222}Rn-PAEC-equilibrium factor F. With quasi-continuous sampling, and so much the better using $\beta\alpha$-spectrometry, the individual member concentrations of the Rn decay chains can be evaluated delay free. Concurrent inline sampling on screens, and free of entrance losses, will also provide the unattached Rn decay product concentrations.

- Table 1. Steady state **sensitivity** of various types of α-spectrometric measuring systems for Rn gas - approximated as detected nuclide α-counts/hour at a Rn concentration of 10 Bq/m^3 (36 Rn atom decays/hour.liter); the Bi/Po α-signals require incorporation in Rn evaluation.

Instrument / α-counts.h^{-1}	^{222}Rn	^{218}Po	^{214}Bi/Po*	^{220}Rn	^{216}Po	^{212}Bi/Po**
Rn track-etch dosimeter	~0.02	~0.02	~0.02	~0.02	~0.02	~0.02

- track-etch environmental monitor° 0 0.02 $<0.3^+$ 0 0 $<4.5^+$
- ½ liter Rn ionisation chamber 12 9 9 12 9 9
- ½ liter electrostatic Rn monitor 0 9 9 0 9 9
- 2 liter/min concentrating on filter 0 80 $<1300^+$ 0 0 $<18000^+$

* delay from $t_{½}$ of ^{214}Pb and ^{214}Bi, and particularly ** of ^{212}Pb and ^{212}Bi need to be taken care of,
° 2 liter/min concentration on filter with collimated track-etch detection (ALGADE)
…$^+$ equilibrium dependable rates from respective decay product concentrations should normally be compensated for.

Note that probably with most measurement systems evaluation algorithms are used that yield concentration values that are not adequately corrected for measurement delay – the systems are generally calibrated only for steady state situations, and thus strictly are not suited for the accurate assessment of concentrations that vary significantly in measuring intervals of the order of respective halflives; alerting to 'data quality' errors, as from some instruments, does not alleviate the situation. The delay effect is due to the time development of the various chain member activities in the instrument subsequent to sample intake. The effect of delays for a halflife up to $t_{½}$ = 3 min (^{218}Po) is generally negligible for diurnal (hourly) measurements, delays for $t_{½}$ up to 30 min (^{214}Pb .. Bi) can be significant for diurnally rapidly changing concentrations, and instrumental response for ^{212}Pb.. ($t_{½}$ = 10.6 h ..) definitely requires appropriate evaluation if diurnal cycles are to be evaluated, irrespective of Rn-gas or Rn-decay product concentration determination.

The calibration of some measurement systems is not always reliable at concentration levels of a few Bq/m^3, making some measurement comparisons rather inaccurate.

Rn concentrations – global and local

The total ^{222}Rn activity in the global atmosphere is in equilibrium with the total ^{222}Rn exhalation from the continental surfaces – as required for compartment balance of source and decay. Since ^{222}Rn exhalation from soil generally is far greater than from the oceans and ice cover, the large-scale lateral distribution of ^{222}Rn over the globe is influenced to a variable degree by off- and onshore movement rates of air masses relative to the ^{222}Rn halflife of 3.8 days.

In the atmosphere the fraction of vertical air mass exchanged (mixed) per unit time, λ_v, is usually much higher than the fraction of ^{222}Rn decay per unit time in the air ($\lambda_v + \lambda_{Rn\text{-}222} \cong \lambda_v$), so that a nearly homogeneous vertical ^{222}Rn concentration (Bq/kg air) can be expected over all altitudes above ground, at a concentration level probably somewhere below 4 Bq/kg air ≈ 5 Bq/m^3 NTP. Only for situations where and when the vertical air exchange is much reduced near the source of ^{222}Rn, i.e. the ground, so that the constant $\lambda_{Rn\text{-}222}$ value becomes competitive with λ_v, can the ^{222}Rn concentration close to the source accumulate to values significantly above the mean concentration, to a local value which depends mainly on the duration and relative residual value of λ_v, and decreases with (vertical) distance from the ground.

Vertical mixing of air λ_v is linked (in a complex way) to differences in wind speed of air layers parallel to the ground, the ground contact layer having zero speed. The diurnal cycle of insolation produces a diurnal cycle of vertical air mixing. During calm weather there may be vertical mixing cycles, parts of which are practically windless so that the usual turbulent, eddy diffusional mixing stops, leaving only molecular diffusion near the ground, a period during which the ^{222}Rn can accumulate there to raised concentrations. The occurrence and duration of such adequately windless, minimal vertical mixing intervals is also strongly dependent on the surrounding topography, the plant or tree cover and structures. An adequately calm interval usually starts late in the afternoon and may last until the onset of turbulent diffusion in the morning, when the raised local concentration near the source is again rapidly diluted to the mean vertical concentration. For diurnal cycles where a lower threshold in wind speed is not crossed, vertical mixing can prevent substantially raised concentrations (to above the vertical mean concentration) near the ground. Stable inversion layers can persist in some locations for days and present the opportunity for still more extended accumulation of the various concentrations.

Over the height of the atmosphere the activities of the short-lived decay chain members of ^{222}Rn are in equilibrium with the ^{222}Rn concentration, except for washout during, and for about an hour after rain or snow. However, when the $\lambda_{Rn\text{-}222}$ value becomes competitive with λ_v near the ground and ^{222}Rn can accumulate near the source to elevated concentrations, then the short-lived decay chain members follow suit with appropriate decay chain timing. This timing results in activity disequilibrium of the chain members and can be measured as activity ratios, a compounded ratio being the ^{222}Rn potential alpha energy concentration equilibrium factor $F_{Rn\text{-}222}$.

Measurement results

In support of the above interpretation hourly measurements were made at 4 measuring sites a few km apart. Over a 20+ day period hourly values of the ^{222}Rn- and the ^{222}Rn-PAE-concentration were taken with 7 different α-spectrometric instruments. As all the data show continuous diurnal cycles with corresponding patterns, only a subset of measurement data is presented in fig. 1 with ^{222}Rn concentration and wind speed . These show particularly two types of diurnal cycles: starting late afternoons of the 7-day period with hardly any wind for part of 24hours (12. to 19. Oct. 2003) and 6 cycles (starting 9.- 11. & 22. 24. & 25.Oct. 2003) selected with at least some wind all during the cycle. Data from an on filter continuously concentrating spectrometer are presented, as this instrument efficiently provides additional ^{222}Rn-decay-chain ratio data (F factor) to corroborate the vertical air mixing model.

The seven diurnal cycles starting Oct. 12.-19. are superimposed in fig. 2a, and the 'always some wind' cycles in fig. 2b; since ^{222}Rn accumulation cycles don't start with minimum concentration at 00h00, the concentration values on diurnal scale >24h are repeated at >0h of the following day. In fig. 3a and 4b the corresponding ^{222}Rn EEC F-factor is shown restricted to $F \leq 1$, as it was determined without measurement delay correction.

Interpretation of measurement results

Comparing the a and b parts of figure 2 shows that only during a diurnal cycle with several hours of practically no wind does the ^{222}Rn concentration build up to an elevated level. If the wind velocity does not go below some minimum, the concentration approximates the general low concentration at higher wind velocity, i.e. with far better vertical mixing, to the low value of the vertical mean concentration.
The diurnal course of the measured F factor corroborates the above explanation: only the excess (above the mean) of freshly accumulated ^{222}Rn near the source can produce a decay chain concentration mixture with an F factor reduced below $F = 1$, as expected higherup.

Discussion and implications of the findings

The mean value of the Rn (decay chain) concentration near the ground is usually considered over one or several months, seasons or years. This value, on the one part, has a more or less steady contribution from the generally low Rn concentration in the upper atmosphere, and at a given site possibly a few very enhanced contributions from local exhalation during individual periods of several hours of minimal vertical air mixing. The mean Rn value over a longer term thus depends on the particular choice of the period with its weather-dependent, site-specific ratio of minimal vertical air mixing intervals to normal mixing time, and during these minimal mixing periods on the Rn exhalation rate from the ground. Only the last term, exhalation, could possibly be, or have been affected by current or past mining activities, and its assessment is blurred (very imprecise) in longer term Rn mean value determinations. Also the Rn exhalation is influenced by precipitation and ground temperature, but the superimposed variability from vertical air mixing usually strongly dominates the variability of long-term mean concentrations.

The foregoing measurements have illustrated that with on filter collecting instruments low outdoor concentrations of decay chain members can be quantified in hourly steps, and they have elucidated the behaviour of outdoor concentrations near the ground. These instruments will soon be operated in an optimal quasi-continuous sampling mode so that the individual concentrations of all short-lived decay chain members can be assessed with instrumental measurement delay corrected. The activity concentration ratios of decay chain members (as well as the derived F factor) are functions of the air exchange in a given compartment mixing model with source and decay. From hourly concentration- plus concentration ratio measurements during a pronounced diurnal cycle(s) of ^{222}Rn- as well as of the ^{212}Pb- decay chain concentrations the ^{222}Rn- and ^{220}Rn-exhalation and the exhalation ratio can thus be determined. Attempts by previous authors to determine, from monthly or longer integrated measurements, a ratio signature of the two decay chains ascribable to possible mining influence was fraught with high imprecision. The high concentration variability in and of diurnal cycles in longer periods, and of the local topography influence on lower levels of vertical air exchange had not been adequately considered. The relative effect of precipitation on local exhalation of ^{222}Rn and ^{220}Rn may need clarification, but the wide-area diurnally resolved exhalation rate and/or -ratio should be a more reliable indicator, than the mean ^{222}Rn-concentration, of possible influence of mining activities in a given area.

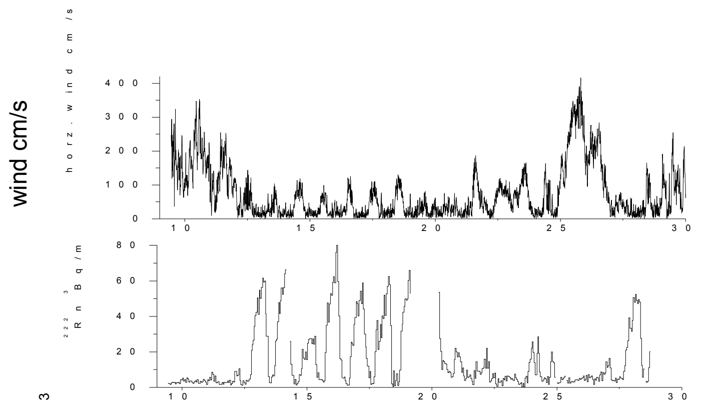
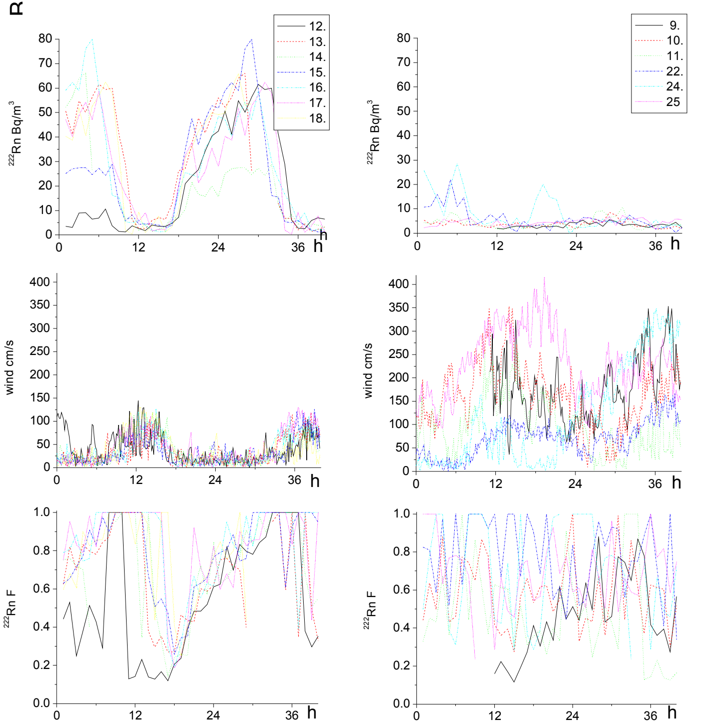


Fig. 1: Measurements 9 - 30 Oct. 2003



a: diurnal cycles starting 00h00 on 12th to 18th Oct

b: diurnal cycles starting 00h00 on Oct 9,10,11,22,24&25

Fig.2 Diurnal cycles selected to show different nature -
a) minimal wind period for ^{222}Rn accumulation @ F low
b) always at least some wind - thus elevated F and low ^{222}Rn

DRAFT

NEW REGULATORY DEVELOPMENTS AND GUIDANCE IN THE EU WITH REGARD TO NORM

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ABSTRACT

A framework for a regulatory system for the control of exposure of workers and members of the public to natural radiation sources was introduced in Council Directive 96/29/EURATOM 13 May 1996. The directive deals with basic safety standards for the protection of the health of workers and the general public against the dangers posed by ionising radiation. In particular Title VII of the directive deals with significant increases in exposure due to natural radiation sources. This applies to “work activities” or industries within which the presence of natural radiation sources leads to a significant increase in the exposure of workers or members of the public and which cannot be disregarded from the radiation protection point of view. In accordance with Articles 40 and 41 of the directive, each Member State is directed to ensure the identification of such work activities and to setting-up the appropriate means for monitoring exposure and applying radiation protection measures as set out in the directive.

To assist Member States with the implementation of the directive in general and Title VII in particular, the Commission has published a number of guidance documents. However, no guidance has yet been developed in relation to discharges from NORM industries. In order to begin to address this, a study was carried out, the results of which have now been delivered. The aims of this study were: to review the regulatory framework within Member States regarding the implementation of Title VII of the directive with respect to effluent discharges; to provide guidance for a realistic dose assessment methodology for NORM discharges and to establish criteria allowing the rapid identification of effluent discharges potentially requiring regulatory control. The results of this study will be considered by the Article 31 Group of Experts with a view to advising the Commission on appropriate guidelines.

In addition, the Commission has awarded a contract with a view to developing a Network for stakeholders involved in NORM issues to share experience and to build a common understanding of the inherent problems and workable solutions. The

Network will aim to identify and promote good practice, to enhance risk awareness and to create a common risk culture between stakeholders. It will act as an archive for relevant documentation that will be available to the members of the Network.

1. INTRODUCTION

The objective of this paper is to provide an update on activities by the European Commission in the domain of NORM and in the context of the Basic Safety Standards Directive (96/29/Euratom). Two recent initiatives in particular are summarised:

- namely the outcome of a study of progress in implementation into national legislation of regulations concerning NORM in Member States (European Commission, 2004)
- a proposal for the creation a network of NORM stakeholders in Europe (NORMNET)

In addition, the conclusions of a recent study, MARINA II (European Commission 2003), as they relate to NORM industries are also presented providing an example of the impact of some NORM industries on the European marine environment. MARINA II was commissioned by the European Commission as part of its ongoing commitment to the OSPAR process.

2. BACKGROUND

2.1 Chapter III of the Euratom Treaty

The Treaty establishing the Atomic Energy Community (Rome, 1957) introduced, at a very early stage of the development of nuclear energy, the need to ensure adequate protection of the health of workers and of members of the public in relation to the dangers arising from ionising radiation. Article 2b of the Treaty lays down that the European Community (EC) shall ‘establish uniform safety standards to protect the health of workers and of the general public and ensure that they are applied’. Chapter III (Health and Safety, Articles 30-39) is concerned with radiation protection, in particular with safety standards (Article 30-33) and specifically with environmental radioactivity (Articles 34-38).

2.2 Basic Safety Standards

The first standards were laid down in 1959 and they have been continuously updated in the light of international guidance (via the International Commission on Radiological Protection (ICRP) on radiation effects and related concepts and taking into account practical experience with national legislation and operational radiation protection. The most recent revision to the standards was adopted in May 1996 (96/29/Euratom). Their implementation in national legislation was scheduled for completion in May 2000.

2.3 The Basic Safety Standards and NORM

The provisions on work activities involving exposures to natural radiation sources are set out in Title VII of the Basic Safety Standards Directive (BSS). Articles 40 and 41 establish a stepwise system in which the Member States are required:

to identify, by means of surveys or by any other appropriate means, work activities which may be of concern,

to set up appropriate means for monitoring exposure in the identified work activities

(as necessary) to implement corrective measures to reduce exposure pursuant to Title IX (Intervention),

to apply all or part of the system of radiological protection for practices, as prescribed elsewhere in the BSS Directive.

The structure of the BSS Directive is such that *a priori* all work activities are within its scope. It is for Member States to identify those work activities that are of concern and that require an appropriate form of regulatory control. Surveys will relate to the characteristics of industries processing materials with (enhanced levels of) naturally occurring radionuclides (NORM).

The approach of Title VII is thus rather general offering flexibility for the Member States to take into account national circumstances. Such flexibility is necessary in view of the fact that in many Member States there may be little experience with the regulation of natural radiation sources.

The economic implications of controls imposed on industries processing raw materials may be such as to require a harmonised policy within the Community. The Group of Experts set up under Article 31 of the Euratom Treaty have recognised this need and have provided technical guidance[1] on the implementation of a system of protection for workers (not only in NORM industries but also for radon in workplaces and for exposure of aircrew to cosmic radiation).

3. REVIEW OF IMPLEMENTATION PROGRESS BY MEMBER SATES

3.1 Context

Following the publication of the BSS Directive, the European Commission funded research to assist Member States in the area of NORM and subsequently published related guidance, in particular RP 95 and RP 122 Part II. Such documents are not

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[1] Recommendations for the implementation of Title VII of the European Basic Safety Standards Directive concerning significant increase of exposure due to natural radiation sources (Radiation Protection 88, 1997, http://europa.eu.int/comm/environment/radprot/88/88.htm).

regulations but guidance and carry no obligations for Member States. Radiation Protection 95 (European Commission, 1999) provides reference levels for identifying those industries for which workers exposure should require regulatory control. Radiation Protection 122 Part II (European Commission, 2001), relates to exemption and clearance and is of particular relevance to the workplace. Significantly, no guidance has yet been developed in relation to discharges.

A limited review of the regulatory framework in EU Member States in relation to the regulation of ‘work activities’ as defined in Title VII has been undertaken as part of the current study. The objective of the study was not a legal review of Member States’ compliance but of the regulation of the impact on the public of work activities and, specifically, of discharge control for such activities. Information gathered for the review consisted of data from recent papers and publications and in particular from the responses by national regulators, or by other national advisory bodies to a questionnaire.

Within the BSS Directive activities involving naturally occurring radionuclides, (not being used for their radioactive, fissile or fertile properties), likely to result in a significant increase in exposure of workers or the public, were defined separately as ‘work activities’.

The main provisions relating to ‘work activities’ are contained in Title VII of the Directive. Under Article 40 these activities should be identified by the Member States. Once identified as of concern, Article 41 states that Member States shall require exposure to be monitored and corrective/protective measures implemented, as necessary, pursuant to part or all of the requirements set out in rest of the Directive in Title IX (intervention) and Titles III (reporting and authorisation), IV (justification and optimisation), V (estimation of effective dose), VI (fundamental principles of radiation protection for workers) and VIII (radiation protection for the public).

Member States have been provided with some guidance in the area by means of the following publication – ‘Radiation Protection 122 Part II – Application of The Concepts of Exemption and Clearance to Natural Radiation Sources’. Two significant conclusions of this report were:

- that for NORM one simple set of levels covering both concepts, exemption and clearance, is appropriate
- that rather than an individual dose criterion, a dose increment in addition to background exposure of the order of 0.3 mSv for workers as well as members of the public is appropriate.

Though one set of values is recommended it is also emphasised that, for exemption, the levels must be fixed allowing industries to decide whether reporting is necessary. However, for clearance some flexibility will be necessary to allow for the best option for waste management and for the specifics of particular industries. So, though the levels may be the same, the concepts remain different requiring separate approaches.

3.2 The Main Findings of the Review

On reviewing the available information it is noted that all EU Member States have acknowledged the issue of ‘work activities’ within their regulatory structure. Often Member States have concentrated in the first instance on the impact on workers. However, Member States appear to be at an early stage in the area of identification of significant exposure to the public from wastes and discharges.

Initial identification of general groups of industries that may be affected based on published reports, has been completed in eleven out of fifteen of the countries with a further four countries currently in the process of their initial identification process (Fig 1). A number of countries are beyond the initial identification stage and have completed detailed studies into the industries within their countries establishing those processes that require regulation. Such countries include Germany, the Netherlands, Finland, Sweden and the UK. Denmark and Greece have completed detailed studies into some industries, but the identification process is still ongoing. In the other Member States where the initial identification process is complete, detailed investigations are either planned or are ongoing.

Three quarters of those States who responded to the questionaire issued as part of the study had regulations relating to NORM, have used the concept of exemption within their legislation (Fig 2 & 3). By restricting regulatory control to those industries, for example, where effective doses could exceed 1 mSv y^{-1}, regulatory resources can be concentrated on those industries of significance.

At present there are no specific discharge controls, specific assessment procedures or constraints for wastes from work activities in the majority of countries. A number of countries including Spain, Ireland, Austria and Sweden indicated an intention to review their discharge controls with respect to NORM wastes in the near future.

There appears to be little radiological control in the area of liquid and aerial discharges specific to the NORM industries. It should be noted that environmental protection measures in place to control particulate emissions and heavy metal releases etc may have the additional benefit of also limiting radiological releases and this was highlighted by Ireland who suggested that they may fall within the scope of their ‘Environmental Protection Act 1992’. Solid waste controls are more common, for example in Germany there are detailed regulations for the disposal of solid material.

3.2.1 Dose limits, constraints and NORM

According to Article 41 (b) of the BSS Directive Member States shall apply radiation protection measures including Title IV, dose limits, as necessary. It can, therefore, be concluded that these dose limits could be applied to NORM.

The current state of application of these concepts in the case of Member States can be summarised as follows:

- In relation to dose criterion for the disposal of solid wastes and NORM residues Greece and Denmark both include a value of 0.3 mSv y^{-1}, equal to the value recommended within RP 122 Part II. However, a number of countries, including Belgium, Germany, Luxembourg and the Netherlands, stated that they did not embed this values due to a mis-match in timing between the release of advice and implementation of legal provisions. The Netherlands use 0.3 mSv y^{-1} effective dose. However, this is the dose criterion for exposure of the public from solid residues containing natural radionuclides - for workers the criterion is 0.1 mSv y^{-1} under normal conditions or 1 mSv y^{-1} under unfavourable but realistic conditions.
- Ireland, Austria and the UK in particular, incorporate the concept of dose constraints within secondary legislation. However, values are not stated in the legislation and are likely to be determined by the relevant regulator as directed by government policy.
- Austria and Denmark do not consider a lower boundary below which further optimisation is no longer required. In Greece dose constraints provided in

their legislation are set within the process of optimisation and so there is no optimisation requirement below dose constraints.

- Finland has a provision within tertiary legislation for dose constraints for exposure from natural radiation in the range of 0.1 to 0.5 mSv y^{-1} which can be applied to effluents as well as solid disposal. However, despite these regulations being in place since 1992 no occasion has arisen, as yet, requiring the application of dose limitation to discharges. In Greece there are no discharge limits because, similarly, as yet no significant liquid or gaseous NORM waste has been found to be present at the identified work activities.
- In Sweden and the UK existing dose constraints are not NORM specific and were largely formulated for the purpose of controlling discharges from practices, nevertheless, they can be used in relation to NORM. However, Sweden is undertaking a review of their controls of natural radiation exposure in view of Title VII of the BSS Directive. Spain and Ireland are also reviewing discharge controls. At present there are no specific discharge provisions.

In conclusion there are few NORM specific discharge controls in place at present and where these do exist, such as in Finland, there have been few occasions when the limits have been applied.

4. THE NORM NETWORK (NORMNET)

4.1 Objectives

The Commission is aware that all of the provisions of Title VII of Council Directive 96/29/EURATOM (13 May 1996) have not yet been fully implemented in practice in all Member States and intends to encourage harmonisation of the approaches used by the Member States. The Commission also wishes to contribute to the circulation of information and to increase the risk awareness of the various stakeholders in relation to NORM. In this context, the Commission wishes to create a ‘NORM Network’. The network will be established as a web-based forum.

The NORM Network aims to provide a tool to:

- Develop links and share expertise between European NORM stakeholders
- Sustain the efforts made in different countries through the exchange of information
- Identify good practice and to promote it
- Enhance risk awareness and create a common risk culture between stakeholders
- To gather and organis documentation made available to the members of the network,
- To preparing periodic summaries of the information
- To provide a basis for recommendations for further action (reports, conference, etc)

Members for the NORM Network will be requested to agree to some terms and conditions. They must be active within the EU, EU accession states and candidate states, Iceland, Liechtenstein, Norway or Switzerland. In particular, members will be those stakeholders who deal with NORM and are involved in the various themes proposed within the Network. They will include regulators (local, national and international organisations), NGOs, consultants and professionals in research and industry.

5. MARINA II

The primary objective of the MARINA II study was to provide an input from the European Commission into the work of the OSPAR Commission in support of the implementation of the OSPAR strategy with regard to radioactive substances. It provides information on radioactive discharges, including those from NORM industries as well as concentrations of radioactivity within the marine environment and an assessment of their impact on humans and marine biota. It follows an earlier MARINA I study [European Communities, 1990], which considered data up to the mid-1980s. The main conclusions of the study with respect to NORM industries discharging into the OSPAR region (North East Atlantic) were:

- The overall discharge of α-emitters into the OSPAR region has remained constant since 1986 due to the discharges from the phosphate industry and the production of oil in the North Sea. By 1999, the estimated discharges of produced water alone contributed 90% of the discharge of α activity into the OSPAR region. Since at least 1981, the discharges of phosphogypsum from the phosphate industry have dominated the collective dose to the population of the European Union. This is because of the higher radiotoxicity of the radionuclides discharged by these industries compared to that of the radionuclides that are discharged from the reprocessing plants.
- The peak collective dose rate from NORM industries occurred in 1984 and was just over 600 man Sv y^{-1}. This collective dose was almost entirely due to discharges from the phosphate industry with the important sources being discharges into Cumbrian waters from the UK and into the North Sea from the Netherlands. Discharges from the phosphate industry, particularly in the UK, were reduced in the 1990s but the phosphate industry is still a major contributor to the collective dose rate.
- Discharges from the oil and gas industry, which made a small contribution over much of the period from 1981 to 1999, have become relatively more important.

In 2000, discharges from the oil and gas industry contributed about 39% to the total collective dose rate from the NORM industries.

- It was found that discharges and collective doses resulting from the production and application of radiopharmaceuticals were negligible in comparison with those from either nuclear reprocessing or oil production. The same applies to discharges from shipyards servicing nuclear submarines in the UK, historic dumping of wastes at sea and submarine accidents.

6. REFERENCES

European Commission, 1990. The Radiological exposure of the population of the European Community from radioactivity in North European marine waters, (Marina I), EUR 12483, Luxembourg.

European Commission, 1999. 'Reference levels for workplaces processing materials with enhanced levels of naturally occurring radionuclides', *Radiation Protection* RP95, Luxembourg.

European Commission, 2001. Practical Use of the Concepts of Clearance and Exemption – Part II Application of the Concepts of Exemption and Clearance to Natural Radioactive Sources, *Radiation Protection* No 122, Luxembourg.

European Commission, 2004. Effluent and Dose Control from European Union Norm Industries – Assessment of Current Situation and Proposal for a Harmonised Community Approach. Radiation Publication RP135, Vol.1 and 2, Luxembourg.

European Commission, 2003. Marina II Update of the MARINA Project on the radiological exposure of the European Community from radioactivity in North European marine waters Annex A: Civil Nuclear Discharges into North European Waters, Radiation Protection RP132, Luxembourg.

Figure 1: Progress in the identification of work activities in Member States

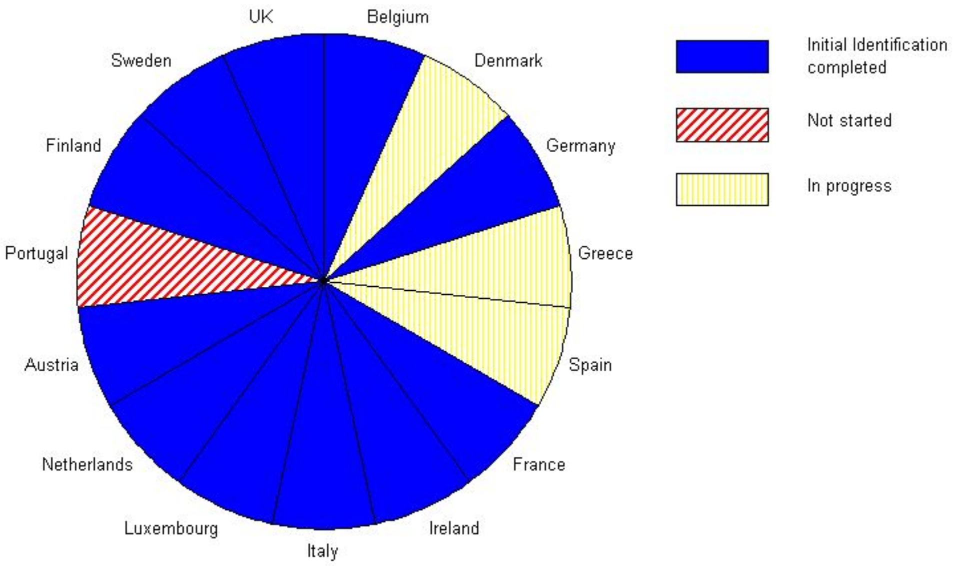


Figure 2: Existence of discharge controls for NORM within Member States

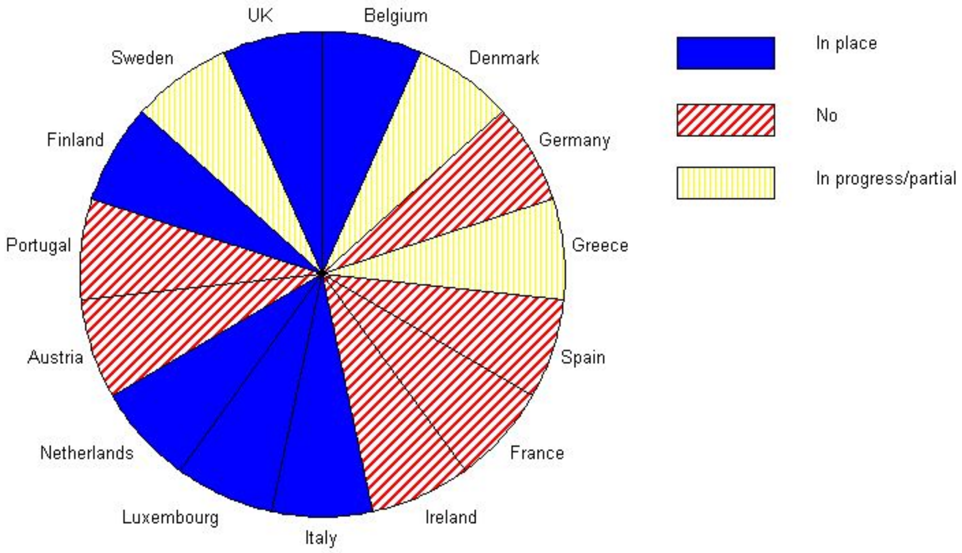
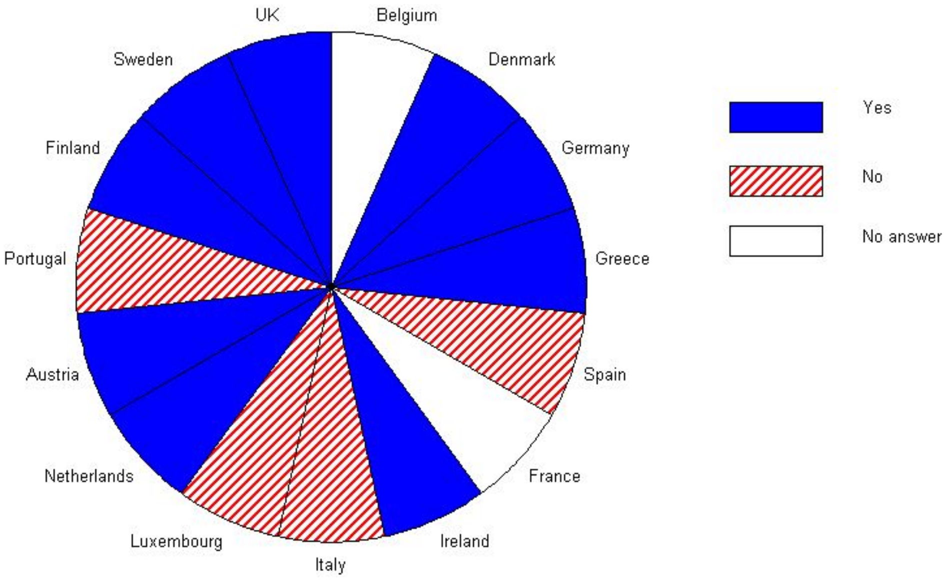


Figure 3: Application of the concept of exemption to NORM within Member States



DRAFT

INDUSTRIES GIVING RISE TO NORM DISCHARGES IN THE EU – A REVIEW

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ABSTRACT

The focus of this paper is the identification of industries giving rise to discharges or residues of naturally occurring radioactive material (NORM) that are potentially significant in terms of public exposure and therefore may require regulatory control as set out in Title VII of EU Council Directive 96/29/Euratom (Basic Safety Standards Directive). The industries have been identified and assessed as part of a study commissioned by the European Commission with a view to assisting Member States in implementing the aforementioned Directive in this area. Information was gathered largely on the basis of data supplied by regulatory authorities in Member States, by means of a questionnaire as well as through published reports and direct contacts with organisations such as trade associations. It is evident that available information on wastes and discharges both in terms of volume and content are limited. Furthermore, there are few reliable monitoring data for NORM radioactive substances probably as a consequence of the absence of previous regulatory control.

The industries considered in this paper include: fossil fuel power stations; oil and gas extraction; metal processing; phosphate processing and production; titanium oxide pigment production; rare earth processes and cement production. A brief description of the processes involved in each is presented including the waste production pathways, activity concentrations, typical emissions and annual throughput, where available.

It is noted that characteristics of discharges and residues, even from the same type of industry and production process, have been found to differ widely because of the variation in raw material used and processing methods. This is particularly pertinent in respect of differences in treatment of liquid wastes and off-gases prior to discharge.

It is possible that for some of the NORM industries studied, controls already in place to prevent non-radioactive pollution may have the additional benefit of controlling the radioactive discharges. However it must also be highlighted that restricting discharges may increase the amount of radioactivity retained in residues such as sludge and dust.

1. INTRODUCTION

The main objective of this paper is to summarize the main findings of the study carried out on behalf of the Commission into those industries giving rise to discharges or residues of naturally occurring radioactive material. The full report of the study – 'Effluent and Dose Control from European Union NORM Industries – Assessment of Current Situation and Proposals for a Harmonised Community Approach' has been published in the Radiation Protection Series of the European Commission's Radiation Protection Unit as RP135 (European Commission, 2004). The interested reader is directed to the full report in order to access the complete data set.

NORM is the acronym for Naturally Occurring Radioactive Material. Most materials contain trace amounts of ^{238}U, ^{235}U and ^{232}Th, however, when these materials are processed, concentration or enhancement of the levels of these radionuclides may occur. Enhancement is said to have occurred when a naturally occurring radioactive material has its composition, concentration, availability or proximity to people altered by human activity (HPS, 2002). NORM can be defined as all naturally occurring radioactive materials where human activities have increased the potential for exposure in comparison to the unaltered situation. However, activity concentrations in the end product may or may not be increased (Vandenhove et al, 2002).

The industries covered by the current review include:

- Fossil fuel power stations;
- Oil and gas extraction;
- Metal processing - iron and steel production in particular but also tantalum and niobium;
- Phosphate industry;
- Titanium oxide pigment production;
- Zirconium and rare earth processes - refractory products and brick manufacture;
- Cement production.

The water industry including waterworks and water purification, has been cited in the past, as an industry giving rise to potentially significant NORM wastes. In a recent report, Hofmann et al, (2000 (a)) focused on the radiological impact due to wastes containing radionuclides from the use and treatment of water and concluded that such wastes did not give rise to concern.

It should be emphasized that characteristics of discharges and residues, even from the same type of industry and production process, have been found to differ widely because of the variation in raw material used, differences in process methodologies as well as differences in the treatment of liquid wastes and off-gas prior to discharge.

It is also possible that existing controls in place to prevent non-radioactive pollution may have the additional benefit of controlling the radioactive discharges from these NORM industries as a by-product of controlling discharges generally. However, it should also be noted that restricting discharges such as those from stacks may increase the amount of radioactive residues contained in solid wastes, sludges and dusts.

A summary of the potentially significant NORM industries together with and identification of waste streams and a statement of the presence or otherwise of the industry in Europe is presented in Table 1.

2. THE INDUSTRIES

2.1 Fossil fuel power stations

Fossil fuels such as coal, lignite, oil and natural gas are used to produce energy by combustion. These fuels contain varying amounts of natural radioactivity often depending on the area from which they are mined or extracted. When coal and oil is burned, the radioactivity is transferred largely to the ash except where volatile radionuclides are released to the atmosphere along with a proportion of the ash. Where 210Po and 210Pb are volatised in the process they may condense on the fly ash. Enrichment factors increase with decreasing particle size. It has been observed that the type of coal used has a very significant effect upon the activity discharged into the environment, as does the plant design (Martin et al, 1997).

The ash content of coal is typically about 16% (smith et al, 2001) with that of peat between 2 to 6% and that of fuel oil at 0.1% the enrichment of the activity concentration from coal to ash is dependant on the ash content but is typically of the order of a factor of seven. Lignite/brown coal has a lower ash content than other coal and this results in a higher enrichment factor, but it has considerably lower activity concentrations (puch, 1997).

The application of coal ash in building materials is regarded as the most significant practice from a radiological point of view because it may affect indoor dose from external radiation and inhalation of radon decay products (unscear 1993).

Liquid wastes may arise from the desulphurisation of flue gases which generates water along with the gypsum. Often the liquid waste is used to carry the ash away and then the slurry is stored in ponds. Alternatively, the water can be recycled to the plant as part of a closed loop (martin et al, 1997). It is unlikely, however, that there is a significant liquid discharge of norm nuclides from fossil fuel power stations. Fly ash emissions from the stack of coal-fired power stations depend on the efficiency of the flue gas cleaning by electrostatic precipitators, scrubbers and desulphurisation systems and so the discharge will vary between plants. It is unlikely that for modern plants there is a significant aerial discharge of norm nuclides from fossil fuel power stations. This is consistent with the conclusion of studies in the uk (smith et al, 2001) and the netherlands where coal fuelled power plants are not considered to have significant aerial discharges. These installations, however, typically install efficient filter systems in order to prevent the aerial discharge of fly ash.

Typical activity concentrations of natural radioactivity in fossil fuels are presented in Table 2 with mean concentrations of radionuclides in certain ashes in Table 3 and typical annual emissions from coal and gas fired power stations in Table 4.

2.2 Oil and gas extraction

According to European Commission 2003 (RP132), there are no ‘typical’ discharges for an oil or gas production plant. Discharges of natural radionuclides depend strongly on the type of reservoir, specific production conditions and numbers of years of exploitation of a reservoir. Production of oil and gas is accompanied by water which is co-produced from the well and so is known as ‘produced water’. The ratio between the rate of water production and oil production is variable, affected by the age of the well and production conditions. The variability is even greater for gas extraction. Produced water contains radionuclides which have been mobilised from the reservoir rocks and in addition to being present in the produced water, they may also be deposited as scales on pipes, valves and vessels. These pipes may be descaled offshore or at onshore descaling facilities. For the most part, releases of NORM from offshore oil and gas production originate from the following:

- Produced water released offshore (^{228}Ra, ^{226}Ra, ^{210}Pb)
- Scale from offshore mechanical descaling released offshore (^{228}Th, ^{228}Ra, ^{226}Ra, ^{210}Pb)
- Scale from coastal descaling site discharged into the sea or disposed on land (^{228}Th, ^{228}Ra, ^{226}Ra, ^{210}Pb)

There is very large variability in radionuclide concentrations in sludges and scales from different wells because of the differences in the nature of the reservoirs and other conditions (Weers et al, 1997). Activity concentrations in sludges and scales vary from virtually zero up to several hundred Bq g^{-1}. Production rates of sludges and scales may vary considerably between installations. While no specific data were available at the time of the current study it is anticipated that the amounts of sludge arising from a given amount of oil production are not significantly lower than for gas production.

A recent study of marine discharges (European Commission, 2003), including discharges from the offshore oil and gas industry, reference ratios for oil and gas production and produced water were estimated together with reference concentration values. However, concentrations of ^{228}Ra, ^{226}Ra and ^{210}Pb in produced water vary between production wells and over the production period, by several orders of magnitude.

Onshore production installations can be assumed to discharge produced water by re-injection into the reservoir, although some installations are known to discharge produced water into a public sewer after pre-treatment. The typical practice for offshore installations is to discharge produced water overboard.

Order of magnitude estimates of discharges of natural radionuclides from offshore oil and gas production platforms are presented in Table 5.

2.3 Metal processing

The basic process by which metals and alloys are produced from metal rich ores is that of smelting. The activity concentrations in the raw materials vary depending on the region of origin. There are currently smelters for aluminium, copper, iron, steel, lead and zinc within the European Union (Kuo et al, 2002). However, tin ore appears to be no longer produced or processed within the EU.

Slags, dross, fly ash, furnace coal ash and scales may be produced as a result of the smelting process. There are also likely to be stack emissions of fly ash and gases; each metal processing involving high temperatures is a potential source of emissions of ^{210}Po and ^{210}Pb to air. The radioactivity of the feedstock or ore is largely transferred to the slag. Although figures were not available for the current paper, zinc production from zinc ore results in cadmium, copper and cobalt-cake and the latter is understood to be enriched in uranium.

2.3.1 Iron and steel production

The main sources of emissions and residues are the installations for production of sinters and pellets from iron ore and the production of iron in blast furnaces from these sinters and/or pellets.

Sinter plants: Iron ore sinters are produced from mixtures of ore, dolomite, cokes and recycled dust. The activity concentrations for most of the radionuclides from the decay chains of ^{238}U and ^{232}Th in the feed mix are in the order of 15 Bq kg^{-1}. ^{210}Po and ^{210}Pb concentrations can be somewhat higher because of the recycling of enriched dust. The sinters are fired with gas and temperatures reached in the combustion zone are in the order of 1400°C. As a consequence ^{210}Pb and ^{210}Po, with boiling points of 1740 and 962°C respectively, are volatilised and condense on dust particles which are carried by the off-gas. Dust from sintering is enriched in ^{210}Po relative to ^{210}Pb and strongly depleted in all other natural radionuclides from the raw materials. The off-gas is cleaned with electrostatic precipitators or high-pressure water scrubbers. The small particles emitted after passing through the cleaning system are enriched in ^{210}Po and to a lesser extent in ^{210}Pb. Emissions to the air depend on the efficiency of the off-gas cleaning system and emissions to water depend on post-treatment of water from the scrubbers.

Pellet plant: Ore preparation for input into the blast furnaces is also carried out in a pelletizing plant. Ore mixes are dried and ground, sieved, mixed with water and bentonite and formed into wet pellets. The pellets are fired into hard pellets and cooled with air. The hot air is fed into the firing zone and to the ore dryer and then fed through low-pressure water dust scrubbers. As in the sinter process ^{210}Po and

^{210}Pb are volatilised and condense on dust particles carried by the off-gas. Solids collected from the wash water are re-fed into the pelletizing process and the water is treated in the biological water treatment system.

Blast furnace: Primary iron is produced from sinters (and pellets), coal and cokes in blast furnaces. They produce iron and slag, both fluid and blast furnace gas carrying dust. Because of the high temperature, ^{210}Pb, and ^{210}Po still present in the feed materials, as well as zinc, are volatilised and condense preferentially on the small particles carried by the gas. ^{210}Pb concentrations in this dust are higher than those of ^{210}Po because the latter radionuclide would have been, to a large extent, already removed in the sintering or pellet process due to its significantly lower boiling point. Wet scrubbers are used to remove the solids from the gas. The coarse material is recycled into the sintering and/or pellet process. The finer fraction, zinc-rich filter cake, is stored for disposal. The cleaned gas is used as fuel elsewhere in the production process or sold as an energy source for electric power production.

Typical activity concentrations of natural radioactivity in certain ores are presented in Table 6 and production figures for selected European metal processing in 2000 are presented in Table 7.

2.3.2 Tantalum and niobium

Tantalum (Ta) is a refractory metal that is highly corrosion resistant, a good conductor of heat and electricity and is used on a large scale in capacitors in all kinds of electronic equipment. Niobium (Nb) is used as an alloying element in steels and super alloys for aircraft turbine engines. The primary source of these elements are the tantalum and niobium bearing ores mined in Australia, Brazil, Canada, Thailand, China and Africa. Prospecting for tantalum is currently underway at sites in Ireland and Finland (Zogbi D, 2002). The minerals in niobium bearing ores (pyrochlore and columbite) contain enhanced levels of the decay chains of ^{238}U and ^{232}Th. Tantalum occurs in combination with niobium and usually with tin, iron, manganese and rare earths. The processing of the ores into metal concentrates, carbides, oxides and metal powder starts with a wet process involving dissolution of the ore with strong acids and liquid-liquid extraction for the removal of impurities. These production facilities are located outside the European Union. A specific source of tantalum is the slag from tin production. The tin slag originates mainly from Thailand and contains enhanced levels of natural radionuclides. Typical concentrations encountered in tin slag from past tin production in the Netherlands and the UK were 4 Bq g^{-1} ^{238}U and 11 Bq g^{-1} ^{232}Th and daughters.

No information was available on natural radionuclides in the tin slag process nor on the processing methods involved. Potentially the processing may involve discharges into the air of ^{210}Pb and ^{210}Po. However, the tin slag is most probably significantly depleted in ^{210}Pb and ^{210}Po because of the high temperatures in the tin smelting process. The solid waste from the tantalum extraction probably contains virtually all of the other radionuclides of both decay chains.

2.4 Phosphate industry

There are four main processes for producing phosphate fertilisers and phosphorus:

- The wet acid process using sulphuric acid (H_2SO_4)
- Hydrochloric acid (HCl) treatment
- Nitric acid (HNO_3) treatment
- Thermal processing

In the sulphuric acid, hydrochloric acid and nitric acid processes the chemical reaction is similar i.e. acidification of the ore. However, the waste products and by-products are markedly different with differing implications for NORM waste production. Across the European Union there have been significant changes in the industry, with a move away from the production of phosphoric acid from phosphate ore and its associated production of large amounts of phosphogypsum. Discharges of phosphogypsum by countries of the EU are in fact historical.

The thermal process uses high temperatures to reduce the phosphate to produce phosphorus, calcium silicate slag and calcinate. Elemental phosphorus plants are in operation in the Netherlands (Hofmann et al, 2000 (b)).

In Europe 90% of the phosphate rock was treated by the sulphuric acid method (Vandenhove, 1999). However, changes in the industry have moved much of the phosphoric acid production, with its associated waste of phosphogypsum, to areas where the phosphate rock is mined i.e. Morocco and other North African countries.

Where the industry remains within the EU, phosphogypsum is largely recycled or stored on land. Approximately 15% of phosphogypsum is recycled into building material (Vandenhove, 1999).

The hydrochloric acid process produces predominately CaF_2 sludge at a rate of 0.5 t for each tonne of processed P_2O_5. This sludge is stored on land where the combination of the radium sulphate precipitate and the calcium fluoride means that the sludge contains 90% of the radium inventory resulting in radium levels of 8 to 10 Bq g^{-1} (Vandenhove, 2002).

There is one phosphor plant within the European Union that uses the thermal process. The refined process in operation at the plant results in no radionuclide enhancement of the silicate slag. However, the calcined dust contains 95% of the ^{210}Pb with a typical activity concentration of 1 000 Bq g^{-1} (Hofmann et al, 2000 (b)).

Indicative activity concentrations of natural radionuclides in ore and waste products from the phosphate industry are presented in Table 8 with estimates of P_2O_5 production in the EU presented in Table 9.

2.5 Titanium oxide pigment production

Titanium oxide pigment is produced from the ores rutile (TiO_2) and ilmenite ($TiO_2 \cdot FeO$). In addition, tin slag may be used as the raw material.

In the original sulphuric acid process ilmenite is dried, ground, mixed with concentrated sulphuric acid and heated until an exothermic reaction commences between the titanium raw material and the sulphuric acid. The solid reaction cake which is formed is composed mainly of titanium and iron sulphates. The reaction cake is dissolved in acid and ferric iron in solution is reduced to the ferrous form in separate reduction tanks using scrap iron as the reducing agent. The reduced solution settles and is filtered to remove un-reacted solids. Much of the iron is removed by cooling and crystallisation into hydrated ferrous sulphate (copperas, $FeSO_4.7H_2O$). After removal of the copperas by centrifugation, the solution is concentrated by vacuum evaporation followed by preferential precipitation of TiO_2 from the iron and titanium basic sulphate ($TiOSO_4$) liquor as white titanium oxihydrate. The titanium oxihydrate is filtered from the dissolved sulphates and extensively washed to remove impurities. The pure white precipitate is calcined in a kiln at about 1000°C to form the TiO_2 crystals of the required size and shape. This traditional production process is being phased out in favour of the cleaner chloride process, but it is unlikely to disappear completely as it is currently also used to produce anastase.

In the chloride process rutile, cokes and chlorine react at about 1000°C to form a mixture of chlorides including the highly volatile $TiCl_4$. The other chlorides are separated from $TiCl_4$ in a series of condensation steps. After purification by distillation the $TiCl_4$ is oxidised to TiO_2 and finished into pigment. About 70% of the European production is from the chloride process.

Typical mean activity concentrations in the rutile are found to be around 400 and 600 Bq kg^{-1} for the ^{238}U chain and ^{232}Th chain radionuclides respectively. However, it is important to emphasise the potential variability of concentrations in such minerals. It is assumed that both chains are in secular equilibrium which is not necessarily the case for synthetic rutile produced from ilmenite in which the iron content of the ilmenite is strongly reduced. The process, involving reductive roasting with coal in a kiln, magnetic separation and acid leaching of the ilmenite (Becher process), not only removes non-radioactive impurities, but may also preferentially remove certain members of the ^{238}U and ^{232}Th decay chains either in the roasting or leaching step. On the basis of this process, the annual activity throughput for a typical TiO_2 production plant is in the order of 40 GBq for each of the nuclides from the ^{238}U chain and 60 GBq for the members of the ^{232}Th chain.

The highly purified TiO_2 pigment is practically free of the natural radionuclides contained in the ore. Emissions to the atmosphere, excluding those of radon, are negligible. Consequently, all radioactivity from the ore appears in the liquid effluent and solid wastes. Solid wastes arise as blow-over of cokes and ore from the reactor and as precipitate from the treatment of acidic solutions of chlorides separated from $TiCl_4$ in the condensation steps. This acidic solution of chlorides contains the majority of the radioactivity contained in the ore. The partitioning of the radionuclides between solid waste and discharged wastewater depends on the treatment of the acidic liquid waste stream. This treatment involves the precipitation of the cations as hydroxides by increasing the pH. Radionuclides of the elements radium and lead tend to remain in solution if the pH endpoint is not high enough.

A summary of the titanium dioxide industry in the European Union including the processes and capacities is presented in Table 10 with typical discharges of natural radionuclides from a TiO_2 pigment plant presented in Table 11.

2.6 Zirconium and rare earth processes

Zircon ($ZrSiO_4$) is a zirconium ore used mainly for high temperature purposes in steel and iron foundries, in refractory materials as well as in fine ceramics. Minor quantities are used as additives in special types of glass. Other uses of zircon and the associated minerals of zirconia and zirconium include abrasive products, catalysts, paints, fuel cladding and structural materials in nuclear reactors (UNSCEAR 1993). Zircon is not mined in Europe but approximately 350 000 tonnes per year are imported into the Union.

Milling which is a physical process involving crushing, grinding and sizing, is carried out at various sites in Europe including the Netherlands, England, Germany, Italy and Spain. The main waste issue associated with the process is that of dust which can be kept to a minimum by good housekeeping. Typically, there is a loss of between 0.1% and 1% of the turnover by this pathway. However, it must be emphasised again that there is a high potential for variability in activity concentrations of natural radionuclides in such minerals.

At zircon mills, comparatively small amounts of waste are produced which are usually disposed of at landfill sites. Quantities of up to 200 t y^{-1} (1% of turnover) have been reported for one plant using dry milling (Scholten, 1996).

In the UK one plant makes fused zirconium for high specification refraction products and dielectrics. The ore Baddeleyite (ZrO_2) is heated in a furnace to extract the zirconium. Sources of waste from this process include liquid effluent from floor washing, dust from the ventilation system and atmospheric discharges from the furnace.

Approximately 20 t y^{-1} of solid powder from the filters is produced from a production of 2000 t of refractory material which is approximately 1% of the feed ore. The waste from floor washings is assumed to be about 20 kg y^{-1}, as are the dust emissions at approximately 5 kg y^{-1} (Martin et al, 1997). Other processes with minor waste production include rare earth glass polish and factories producing refractory bricks where again the waste is likely to be floor washings.

Zirconium ore processing locations and capacity in Europe are summarized in Table 12 and mean activity concentrations of natural radionuclides in zircon and Baddeleyite are summarized in Tables 13 and 14 respectively.

2.7 Ceramics and brick production

The firing temperature of the ovens used in the production of bricks and roofing tiles is between 1000 and 1200°C. The feed clays usually have concentrations of the radionuclides from the decay chains ^{238}U and ^{232}Th in the order of 35 Bq kg^{-1}.

Between 40 and 100% of the ^{210}Po is volatilised in the firing process. The fraction of the throughput of ^{210}Po emitted depends on the extent of the off-gas cooling and cleaning to abate dust and HF emissions.

An upper estimate of the aerial discharge of ^{210}Po from a brick factory can be based on the following assumption: typical production 30 kt y^{-1}, average concentration in clay 35 Bq kg^{-1}, volatilisation 100%, trapping in off-gas 0%. The maximum annual emission for such a plant is 1 GBq.

Italian ceramics is probably the largest consumer of zircon in Europe. Italy imports about 170 000 tonnes per year of zircon sands of which 70% is used in the ceramic industry (Trotti, 2002). However, the zirconium is fixed in the glaze.

2.8 Cement production

Production of cement involves the calcining and sintering of blended and ground raw materials, typically limestone, clay or shale to form clinker (partially fused residues). This clinker burning takes place at a temperature of 1450°C in kilns. The clinker is ground and mixed with small amounts of gypsum to make cement. In addition, blended cements are produced from cement clinker with blast furnace slag and fly-ash. Large cement plants produce in the order of 4 000 t of cement per day (1.5 Mt y^{-1}). Production capacities for cement production plants in the EU are presented in Table 15.

Because of the very high temperature of the raw materials in the kilns, volatilisation of ^{210}Po and ^{210}Pb is the main potential source of aerial discharge. Estimates on ‘typical’ discharges provided in UNSCEAR 2000, Annex B, are based on Leenhouts et al., 1996, and are reproduced in Table 16. In the figures quoted, the fact that blast furnace slag which can be used in blended cements, as mentioned above, is considerably depleted in ^{210}Pb and ^{210}Po has been taken into account. No other source of activity emission data has been identified.

Annual aerial discharges for a 'typical' cement plant are presented in Table 16. The discharge figure for ^{210}Po is based on the assumption that 50% of the polonium escapes from the thermal process in analogy with the assumption used for the production of bricks and roofing tiles.

3. REFERENCES

European Commission, 1999. 'Reference levels for workplaces processing materials with enhanced levels of naturally occurring radionuclides', *Radiation Protection* No 95, European Commission.

European Commission, 2004. Effluent and Dose Control from European Union Norm Industries – Assessment of Current Situation and Proposal for a Harmonised Community Approach. Radiation Publication RP135, Vol.1 and 2, Luxembourg.

European Commission, 2003. *Marina II Update of the MARINA Project on the radiological exposure of the European Community from radioactivity in North European marine waters Annex A: Civil Nuclear Discharges into North European Waters,* Radiation Protection No 132, Luxembourg.

Harvey MP., Hipkin J., Simmonds JR., Mayall A and Cabianca T., 1994. *Radiological Consequences of Waste Arising with Enhanced Natural Radioactivity Content from Special Metal and Ceramic Processes,* EUR15613EN, European Commission.

Health Physics Society (HPS), 2002. http://www.hps.org.

Hedvall R., 1997. *Activity Concentrations of Radionuclides in Energy Production from Peat, Wood Chips and Straw,* Lund University, Sweden.

Hofmann J., Leicht R., Wingender H J and Wörner J., 2000 (a). *Radiological Impact due to Wastes containing Radionuclides from Use and Treatment of* Water, EUR 19255, European Commission.

Hofmann J., Leicht R., Wingender HJ and Wörner J., 2000 (b). *Natural Radionuclide Concentrations in Materials Processed in the Chemical Industry and the Related Radiological Impact*, EUR 19264, European Commission.

Kuo C., Levine R., Newman H., Steblez W., Wallace G and Wilburn D., 2002. 'The Mineral Industries of Europe and Central Eurasia', *US Geological Survey Minerals Yearbook 2000,* http://minerals.usgs.gov/minerals/pubs/country/europe.html.

Leenhouts H.P., Stoop, P., van Tuinen S.T., 1996. *Non-nuclear industries in the Netherlands and radiological risks*, Report No 610053003, National Institute of Public Health and the Environment.

Martin A., Mead S and Wade BO., 1997. *Materials containing natural radionuclides in enhanced concentrations,* EUR 17625, EC DG-Environment, Nuclear Safety and Civil Protection.

O'Dea J and Dowdall M., 1999. 'Spatial Analysis of Natural Radionuclides in Peat Overlying a Lithological contact in Co Donegal, Ireland', *Journal of Environmental Radioactivity*, Elsevier Science, Vol. 44, pp. 107-117.

Penfold J S S., Mobbs S F., Degrange J P and Schneider T., 1999. *'Establishment of Reference Levels for Regulatory Control of Workplaces where Materials are Processed which contain Enhanced Levels of Naturally-Occurring Radionuclides'* Radiation Protection No 107, European Commission.

Puch, K.-H., vom Berg, W., Keller, G., 1997. 'Radioactivity of combustion residues from coal fired power plants', *Proc. Int. Symp. On Radiological Problems with*

Natural Radioactivity in the Non-Nuclear Industry, Amsterdam, 08-10 September 1997.

Roskill Information Services Ltd, 1995. *The economics of zirconium*, 8th Edition.

Scholten L C., 1996. *Approaches for regulating management of large volumes of waste containing natural radionuclides in enhanced concentrations,* EUR 16956, EC DG-Environment, Nuclear Safety and Civil Protection.

Smith KR., Crockett GM., Oatway WB., Harvey MP., Penfold JSS and Mobbs SF., 2001. *Radiological Impact on the UK Population of Industries Which Use or Produce Materials Containing Enhanced Levels of Naturally Occurring Radionuclides: Part I: Coal-fired Electricity Generation,* NRPB-R327, NRPB.

Trotti F., Bucci S., Belli M., Colombo G., Dalzocchio B., Fusato G., Maggiolo S., Nava S., Svegliado G and Zampieri C., 2002. 'Preliminary Identification of Work Activities Involving NORM in Italy', *NORM III Conference*, Brussels.

United Nations Scientific Committee on the Effects of Atomic Radiation 1993 (UNSCEAR 1993), *Ionizing Radiation: Sources and Biological Effects,* Report to the General Assembly, with Scientific Annexes, United Nations, New York, 1993. Annex A: Exposures from Natural Sources of Radiation, Par. 157, pp. 57-58.

United Nations Scientific Committee on the Effects of Atomic Radiation 2000 (UNSCEAR 2000), *Ionizing Radiation: Sources and Biological Effects,* Report to the General Assembly, with Scientific Annexes, Volume I: Sources. United Nations, New York, 2000, Annex B: Exposures from Natural Radiation Sources, Table 28.

Vandenhove H., Zeevaert T., Bousher A., Jackson D., Lambers B., Jensen P H., 1999. *Investigation of a possible basis for a common approach with regard to the restoration of areas affected be lasting radiation exposure as a result of past or old practice or work activity CARE,* Radiation Protection No 115, European Commission.

Vandenhove H., Paridaens J and Vanmarcke H., 2002. 'European sites Contaminated by residues from the ore extraction and processing industries including a case study for Flanders', *IBC 2nd International Conference on Natural Radiation and NORM*, London, 22-23 April.

Weers AW., Pace I., Strand T., Lysebo I., Watkins S., Sterker T., Meijne EIM., Butter KR., 1997. *Current Practice of dealing with natural radioactivity from oil and gas production in EU Member States*, EUR 17621, Nuclear Science and Technology Report, European Commission.

Zogbi D., 2002. 'TheTantalum Supply Chain: 2000 – 2001' *MarketEye*, 14 January http http://www.ttiinc.com/object/ME_Zogbi20020114.html

Table 1: Summary of potentially significant NORM industries

Industry or work activity	Potentially significant solid residues?	Potentially significant liquid discharges?	Potentially significant aerial discharge?	Is such a facility present in EU Member State?														
				B	DK	D	EL	E	F	IRL	I	L	NL	A	P	FIN	S	UK
Onshore oil/gas	Yes, sludges, scales	Yes, if discharged but no if liquids are re-injected	No	-	Yes	Yes	-	-	Yes	-	Yes	No	Yes	Yes	-	-	No	Yes
Offshore oil/gas	Yes, sludges, scales	Yes, produced water, scales	No	-	Yes	Yes	Yes	Yes	No	Yes	Yes	No	Yes	-	No	-	No	Yes
Phosphoric acid	Yes, if phosphogypsum is stockpiled	Yes, if phosphogypsum is discharged	No	Yes	-	-	Yes	Yes	Yes	-	-	-	-	-	-	-	-	-
Phosphate fertiliser[2]	Yes/no, depending on process	Yes/no, depending on process	No	Yes	Yes	Yes	Yes	Yes	Yes	-	Yes	-	Yes	-	Yes	Yes	Yes	-
Thermal phosphorus	Yes, calcined dust and slag	Yes, ^{210}Po, ^{210}Pb	Yes, ^{210}Po, ^{210}Pb		-	-	-	-	-	-	-	-	Yes	-	-	-	-	-
TiO$_2$ pigment	Yes, solids from liquid waste treatment	Yes/no depending on process	No	-	-	Yes	-	Yes	Yes	-	Yes	-	Yes	-	-	Yes	-	Yes
Steel	Yes, blast furnace and sinter dust	Yes/no depending on waste water treatment	Yes, ^{210}Po, ^{210}Pb	Yes	Yes	Yes	Yes	Yes	Yes	-	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Cement	No	No	Yes, ^{210}Po, ^{210}Pb	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

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[2] Include production with phosphoric acid produced elsewhere

Coal fuelled power plants	Bottom and fly ash	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Bricks and roofing tiles	No	No	Yes, ^{210}Po	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Tin smelters (closed down)	Slag, slag wool, historical	No	Yes, ^{210}Po, ^{210}Pb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Metal extraction from tin slag	Yes, slag	No	Yes, ^{210}Po, ^{210}Pb	-	-	Yes	-	-	-	-	-	-	-	-	-	-	-	-
Lead/Zinc smelter	Yes, cobalt-cake	No	Yes, ^{210}Po, ^{210}Pb	Yes	-	Yes	Yes	Yes	Yes	-	Yes	-	Yes	-	Yes	Yes	Yes	Yes
Copper smelter	NK	No	Yes, ^{210}Po, ^{210}Pb	Yes	-	Yes	-	Yes	Yes	-	-	-	-	-	-	Yes	Yes	-

Table 2: Typical activity concentrations of natural radioactivity in fossil fuels

Material	^{238}U series (Bq kg^{-1})	^{232}Th series (Bq kg^{-1})
Coal (global av.) [1]	20	22
Natural gas [2]	340 Bq m^{-3} (^{222}Rn)	-
Peat (global av.) [3]	40	-

[Scholten 1996 [1]; UNSCEAR 2000 [2]; O'Dea and Dowdall, 1999 [3]]

Table 3: Arithmetic mean of activity concentrations of radionuclides in certain ash (Bq kg^{-1})

Material	^{238}U	^{232}Th	^{228}Th	^{228}Ra	^{226}Ra	^{210}Pb	^{210}Po	^{40}K
Escaping fly ash (coal)	200	70	110	130	240	930	1700	265
Bottom ash/ fly ash (coal) [1]	240/200	240/200			240/200	151/220	138/220	653/670
Peat fly ash [2]	268-1048				<215			<1480

[Leenhouts 1996 [1]; Hedvall, 1997 [2]]

Table 4: Annual emissions (GBq) by 'typical' coal and gas-fired power stations

Plant	**^{238}U**	**^{232}Th**	**^{226}Ra**	**^{222}Rn**	**^{210}Pb**	**^{210}Po**
Coal-fired power plant (600 MW e)	0.16	0.08	0.11	34	0.4	0.8
Gas-fired power plant (400 MW e)	-	-	-	230	-	-

[UNSCEAR 2000 from Leenhouts, 1996]

Table 5: Order of magnitude estimates of discharges of natural radionuclides from offshore oil and gas production platforms

	Assumed annual oil production (10^3 m^3)	Annual water discharge (10^3 m^3)	^{228}Ra and ^{226}Ra (Bq l^{-1})	^{228}Ra and ^{226}Ra (GBq y^{-1})		
Oil	**1 000**	**3 000**	**10**	**30**		
	Assumed annual gas production (10^6 m^3)	Annual water discharge (10^3 m^3)	^{226}Ra (Bq l^{-1})	^{226}Ra (GBq y^{-1})	^{228}Ra and ^{210}Pb (Bq l^{-1})	^{228}Ra and ^{210}Pb (GBq y^{-1})
Gas	**3 000**	**150**	**10**	**1.5**	**5**	**0.75**

NB It should be noted that the actual annual discharges at a given platform in a particular year may be quite different from the figures derived from normalised data. Discharges of ^{210}Pb from oil producing platforms have not been estimated, as the radium isotopes are likely to be the dominant radionuclides in the discharges. However, ^{210}Pb cannot be assumed to be absent.

Table 6: Typical activity concentrations of natural radioactivity in certain ores (Bq kg^{-1})

Ore	**^{238}U**	**^{232}Th**
Bauxite (aluminium)	37 - 530	41 - 527
Iron ore [1]	<50	<50
Pyrochlore (ferro-niobium) [2]	6 000 – 10 000	7 000 – 80 000
Tin ore [2]	1 000	300

[Scholten, 1996 [1]; European Commission, 1999 [2]]

Table 7: Production figures (kt) for selected European metal processing activities in 2000

Country	Iron and Steel		Aluminium		Copper[3]	Lead[1]	Tin[1]	Titanium	Zinc[1]
	Pig iron[4,5] and direct-reduced iron	Crude steel[6]	Alumina	Primary Metal	Primary (refining)	Primary (refining)	Primary (smelting)	Metal Sponge	Primary (smelting)
	Metal Content	Gross Weight	Quantity	Quantity	Metal content	Quantity	Quantity		Quantity
Belgium	8 472	11 637	0	0	236	98	0	0	252
Denmark	0	783	0	0	0	0	0	0	0
Germany	30 846	46 376	600	644	335	210	0	0	325
Greece	0	1 056	600	163	0	0	0	0	0
Spain	4 059	15 844	1 200	366	265	0	0	0	391
France	13 661	21 002	400	441	0	100	0	0	348
Ireland	0	375	1200	0	0	0	0	0	0
Italy	11 223	26 544	950	190	0	75	0	0	168
Luxembourg	0	2 571	0	0	0	0	0	0	0
Netherlands	4 969	5 667	0	302	0	0	0	0	215
Austria	4 318	5 725	0	0	2	0	0	0	0
Portugal	382	1 060	0	0	0	0	0	0	4
Finland	2 983	4 096	0	0	100	0	0	0	223
Sweden	3 146	5 227	0	100	105	38	0	0	0
UK	10 989	15 306	100	305	1	166	0	0	99
EU-15	95 048	163 269	5 050	2 511	1 044	687	0	0	2 025

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[3] Primary production also includes undifferentiated (primary and secondary) production for those countries listed

[4] Pig iron is primary iron melted into a standard pyramidal mould or trapezoidal mould, ~ 4.5 and 6.5 kg respectively.

[5] Primary iron production (blast furnace iron) figures are those relevant to emissions and residues.

[6] Crude steel can be produced from primary iron and scrap in a basic oxygen furnace (converter) or from recycled steel in an electric arc furnace. Crude steel production figures are therefore higher than primary iron production figures as the latter are included in the former.

Table 8: Indicative activity concentration in ore and waste products of the phosphate industry

MATERIAL/PROCESS	Radionuclide	Activity Concentration Bq kg^{-1}
Ore[7] [1]	^{238}U+	1 400
	^{232}Th	160
	^{226}Ra+	1 400
	^{210}Pb+	1 400
Sulphuric Acid Process		
Phosphogypsum [1]	^{238}U+	200
	^{232}Th	17
	^{226}Ra+	850
	^{210}Pb+	200
Hydrochloric Acid Process		
Calcium Fluoride (solid) with radium sulphate precipitate (from $BaCl_2$ precipitate step) [2]	^{226}Ra	8 000-10 000
Calcium Chloride (effluent) [2]	^{226}Ra	2 Bq/l
Nitric Acid Process		
Calcium carbonate (recycled)	NK	NK
Thermal Process		
Calcium Silicate Slag [1]	^{238}U+	2 700
	^{232}Th	310
	^{226}Ra+	2 300
	^{210}Pb+	270
Calcined dust [1]	^{210}Pb+	1 600 000

[Penfold, 1999 [1]; Vandenhove et al, 2002 [2]]

NB The above data are as cited in the source material and may be for the selected chain and radionuclide only.

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[7] It is important to note that phosphate ore of igneous origin is lower in radioactivity than that of sedimentary origin and the range of ^{238}U+ measured in ores is quoted in Penfold et al, 1999 as between 40 – 5000 Bq kg^{-1}.

Table 9: Estimate of P_2O_5 production in the European Union

Country	P_2O_5 Production		Phosphate Fertilizer Production	
	kt y^{-1}	% of total EU	kt y^{-1}	% of total EU
Belgium/Luxembourg	270	14	340	14
Germany	0	0	220	9
Greece	200	11	120	5
Spain	530	28	180	7
France	250	13	930	39
Italy	250	13	330	14
Netherlands	120	6	290	12
Austria	55	3	-	-
Finland	240	12	-	-
Total EU	1 900	100	2 410	100

[Hofmann et al, 2000 (b)]

Table 10: Titanium dioxide industry in the European Union for 2000/2001

Country	Site	Company	Process	Capacity (10^3 t y^{-1})
Belgium	Langerbrugge Antwerp	KRONOS Kerr-McGee	chloride sulphate	69 NK
Germany	Uerdingen Leverkusen Leverkusen Nordenham Duisburg	Kerr-McGee KRONOS KRONOS KRONOS Sachtleben	sulphate sulphate chloride sulphate sulphate	130 30 100 62 100
France	Le Havre Thann Calais	Millennium Millennium Huntsman Tioxide	sulphate sulphate sulphate	110 28 100
Italy	Scarlino	Huntsman Tioxide	sulphate	80
Netherlands	Rotterdam	Kerr-McGee	chloride	80
Finland	Pori	Kemira Pigments	sulphate	130
United Kingdom	Greatham Grimsby Grimsby	Huntsman Tioxide Huntsman Tioxide Millennium	chloride sulphate ?	80 80 150

Table 11: Typical discharges of ^{228}Ra, ^{226}Ra, ^{210}Pb, and ^{210}Po in acidic liquid effluent from TiO_2 pigment plant with an annual production of 90 000 t using the chloride process.

Nuclide	GBq y^{-1}
^{228}Ra	38
^{226}Ra	22
^{210}Pb	9
^{210}Po	3

NB Average concentration in the rutile 0.4 and 0.6 Bq kg^{-1} for ^{238}U sec and ^{232}Th sec.

Table 12: Zirconium ore processing in Europe

Country	Quantity (kt y^{-1})
Belgium/Luxembourg	3
Germany	45
Greece	-
Spain	52
France	40
Italy	98
Netherlands	-
Austria	-
Finland	-
EU-15	238

[Roskill, 1995]

Table 13: Radioactivity content of zircon in Bq kg^{-1}

	^{238}U	^{232}Th	^{226}Ra
Average	6 800	11 000	8 300

[Scholten, 1996]

Table 14: Radioactivity content of Baddeleyite in Bq kg^{-1}

	^{238}U	^{232}Th	^{228}Th	^{228}Ra
Baddeleyite	7 000	300	200	6 000

[Harvey et al, 1994]

Table 15: Cement production in EU Member States in 1998

Country	Cement produced 10^3 t
Belgium	8 000
Denmark	2 528
Germany	36 610
Greece	15 000
Spain	27 943
France	19 500
Ireland	2 000
Italy	35 000
Luxembourg	650
Netherlands	3 200
Austria	3 850
Portugal	9 500
Finland	903
Sweden	2 105
United Kingdom	12 409
EU-15	179 198

Table 16: Annual aerial discharges for a ‘typical’ cement plant with a 2000 kt y^{-1} output of different types of cement

Nuclides	GBq
^{238}U	0.2
^{228}Th	0.05
^{226}Ra	0.2
^{222}Rn	157
^{210}Pb	0.2
^{210}Po	78
^{40}K	0.4

[Leenhouts et al, 1996]

THE RAPID IDENTIFICATION OF NORM DISCHARGES REQUIRING REGULATORY CONTROL –A POSSIBLE SCREENING METHODOLOGY

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ABSTRACT

The European Commission (EC) is mindful of the potential difficulties for national regulators in implementing a process of regulatory control as set out in Title VII of EU Council Directive 96/29/Euratom (Basic Safety Standards Directive) for NORM industries discharging into the environment. As a consequence, the EC commissioned a study to identify possible procedures for the rapid identification of such industries or work activities where members of the public are potentially exposed, with a view to producing guidelines. The results of the study are presented in this paper.

It is well understood that there is no simple relationship between discharge rate from a NORM industry and dose to members of the public. However, with respect to regulatory control, a detailed site-specific analysis may not be warranted when, on the basis of a conservative approach, it can be concluded that the discharges are of no radiological significance. This introduces the idea of NORM discharge screening levels which may be defined as estimates of the amount of activity discharged to the environment, which, if not exceeded, mean that it is very unlikely that members of the public would receive an effective dose above a defined dose criterion. NORM discharge-screening levels can be defined for each NORM release route and would be calculated using deliberately cautious assumptions. The derivation of such screening levels would comprise the following steps: definition of reference discharge situations; choices of models, exposure pathways and parameters; derived doses per unit discharge rate; dose criteria for screening levels and finally, discharge screening levels.

In this paper, discharge-screening levels are derived and presented. It is unlikely that below these levels a more detailed site-specific radiological assessment of the discharges would be warranted. It is recommended that a dose criterion be chosen for the screening level that is below the dose constraint for the facility. If discharge-screening levels are exceeded it is recommended that regulatory bodies verify the actual level of discharge, re-examine discharge conditions such as stack height or river flow, re-examine the existence of assumed exposure pathways and decide on the need for site-specific assessment.

Background

Aspects of radiation protection in the field of NORM are covered in the European Basic Safety Standards (European Council, 1996) in Title VII. A study has been completed on this topic in 2003 with the title “Effluent and Dose Control from European Union NORM Industries – Assessment of Current Situation and Proposal for a Harmonised Community Approach”. It has been published in the Radiation Protection Series of the European Commission’s Radiation Protection Unit (DG TREN.H.4) as RP 135 (EC, 2004; two volumes) and can be downloaded from the unit’s website http://europa.eu.int/comm/energy/nuclear/radioprotection/index_en.htm. Within this Conference Tom Ryan covers general aspects of EC NORM policy (Ryan et al, 2004a) and gives a review over NORM industries in the EU (Ryan et al, 2004b). This paper addresses a possible screening methodology.

Introduction

The discharges into air and water from NORM industries vary considerably with respect to the radionuclides discharged, the effective height of the stacks for aerial discharges and the characteristics of the receiving aquatic environment for liquid discharges. Radiation exposure of members of the public resulting from these discharges involves many exposure pathways and the level of exposure per unit discharge rate depends on quite a number of site-specific conditions. Consequently, no simple and general relationship exists between discharge rate and dose to members of the public. On the other hand, detailed site-specific analysis is not warranted when, on the basis of a generalised and conservative approach, it can be concluded that the discharges are of no radiological significance.

NORM discharge "screening levels" are, therefore, defined as

estimates of the amount of activity discharged to the environment from a NORM plant, which, if not exceeded, mean that it is very unlikely that members of the public would receive an effective dose above a defined dose criterion.

Norm discharge screening levels can be determined for each norm release route i.e. To atmosphere, rivers and the marine environment. Such screening levels are calculated using deliberately cautious assumptions such that compliance with them would ensure virtual certainty of compliance with a typical dose constraint.

The derivation of the discharge screening levels comprises the following steps:

- definition of reference discharge situations,
- choices on models, exposure pathways and parameter values,
- derived doses per unit discharge rate,
- dose criteria for screening levels,
- discharge screening levels.

It should be kept in mind that large uncertainties and variabilities may be involved in some of these steps.

The approach used in the study in deriving screening levels for discharges is similar to the methodology described in (NCRP, 1996), although it uses more sophisticated models. The main features of the approach of the NCRP are:

- the derived screening levels serve to assess compliance with environmental standards (limiting values);
- doses estimated by screening are not intended to represent estimates of actual doses to individuals;
- simple models should always be applied first;
- models and parameters are chosen so as to produce conservative estimates of doses;
- sophisticated models are not needed if compliance with environmental standards can be demonstrated on the basis of the screening models;
- screening can be carried out for aerial discharges and for liquid discharges into fresh surface water and marine surface water;
- screening can be carried out at two or three different levels of conservatism in the approach.

The systematic approach

Reference discharge situations have been defined for atmospheric releases (effective stack heights of 10 m, 50 m, 100 m and 200 m to cover a wide range of applications) and for discharges to rivers (large, medium and small rivers with flow rates between 500 and 2.5 $m^3\ s^{-1}$). For releases to the marine environment a similarly straightforward method cannot be applied. Therefore for both, off-shore releases and on-shore releases, scenarios have been chosen and are presented here, that may not necessarily represent a conservative approach. Thus, for discharges to the marine environment a more detailed study of the actual situation is warranted.

Models, pathways and parameters: The screening levels have been calculated for continuous, uniform discharges of radionuclides to the environment (annual discharges, assumed to continue for 50 years; ingrowth of radioactive progeny included).

For **atmospheric releases** the following exposure pathways have been taken into account: external exposure to the plume and to deposited activity; internal exposure due to inhalation of radionuclides from the plume and resuspended activity and ingestion of food produced on land contaminated by the plume. For release heights up to 100 m, a Gaussian dispersion model was used (part of PC CREAM; Mayall et al, 1997); for 200 m the more complex Atmospheric Dispersion Modelling System (ADMS; Carruthers et al, 1994) was used. Doses were calculated assuming basically 100 % occupancy at 500 m from the release point and that 50 % of the consumed food was grown locally.

The exposure pathways for **river discharges** considered were ingestion of untreated river water and of fish, and external gamma exposure from river bank sediments. The model used (PC CREAM) assumes a discharge into a 1 km compartment of the river and complete mixing. Downstream transport of radionuclides in solution, with suspended sediment and in river bed sediment is modelled as well as sedimentation itself.

For **releases to the marine environment** the exposure pathways considered were consumption of fish, crustaceans and molluscs, and external exposure to beach sediment. The model (Poseidon; Lepicard et al, 1998) used two of the boxes developed for the MARINA project (EC, 2003), namely, the boxes ‘North Sea N’ and ‘Baie de la Seine’ as examples. They differ in volume by a factor of 200. Within the vertical compartments of the boxes homogeneity is assumed. The dispersion of radionuclides released into the box is described by water exchange with adjacent compartments, by exchange of radionuclides between dissolved and particulate state via sorption processes and by remobilisation from the bottom sediments into the water layers due to bioturbation and diffusion. The prediction of the radionuclide concentration in marine biota is based on the steady-state approach which assumes a constant equilibrium between the concentration of dissolved radioactivity in water and in marine organisms. For dose calculations the habit data for critical groups were used rather than those for average adult consumers.

Due to the relatively small difference compared to children only the adult age group has been considered as reference group. The dose coefficients for ingestion and inhalation have been taken from the European Basic Safety Standards Directive (European Council, 1996).

Based on these assumptions and conditions the **doses per unit discharge rate** were determined. They are tabulated in the complete study report (EC, 2004).

To define **screening levels of discharge rate** one firstly has to chose a level of annual dose above which the discharge is regarded as potentially of radiological significance (and hence would require more detailed assessment). The choice of such a dose criterion is not straightforward. In the study the screening levels are intended ultimately to identify NORM discharges that definitely should not be regulated or, the other way around, to identify discharges that may be of potential radiological significance and would require a more detailed and possibly site specific assessment. In this case it seems sensible to choose a dose criterion for the derivation of the screening levels that is below the dose constraint (which often is taken as 300 µSv y^{-1}), e.g. in the range 10 - 100 µSv y^{-1}. Therefore, the figures given in the study report and presented below show screening levels for 10, 100 and 300 µSv y^{-1}. For rough comparison, the figures include “typical” discharges as estimated in the full report (EC, 2004).

Use of screening levels

The screening levels are intended for screening purposes and have been calculated using a set of generic assumptions. For discharges below the screening levels there is unlikely to be a reason for a more detailed and site-specific radiological assessment of the discharge. Above the levels – although this does not necessarily imply that the dose criterion will be exceeded – such a detailed analysis is advised. In practice, discharges of more than one radionuclide will occur. Account must be taken of exposures from all radionuclides discharged. If the sum of the ratios for each nuclide discharged divided by the appropriate screening level is less than or equal to one then the total discharge is below the screening level. For some sites it is possible that radionuclides will be discharged by more than one route, for example, discharges to atmosphere and to a local river may occur from the same location. In this case the critical group for the different discharge routes is unlikely to be the same and so summing fractions of the screening level may be overly cautious. If a site-specific dose assessment is required then a more realistic approach could be adopted where account is taken of exposure from all routes using a combination of critical group and average habits. In industrialised areas several sources may discharge into the atmosphere or into the same river. The higher the screening level dose criterion that is chosen, the greater the chance that exposures of the same critical groups to the combined sources may approach or exceed the dose constraint or dose limit.

The derived NORM discharge screening levels in GBq y^{-1} are estimates of the amount of activity discharged to the environment from a NORM plant, which, if not exceeded, mean that it is very unlikely that members of the public would receive an effective dose above a defined dose criterion. A dose criterion should be chosen for the screening levels that is below the dose constraint, e.g. in the range 10 - 100 μSv y^{-1}.

The screening levels of discharge provided in Table 1 for aerial and Tables 2 to 3 for river discharges are based on a screening level dose criterion of 300 μSv y^{-1}. Such screening levels are calculated using deliberately cautious assumptions such that compliance with them would ensure virtual certainty of compliance with the dose constraint. For marine discharges the figures given in Table 4 are only examples, rather than 'recommended' screening levels.

Derived discharge screening levels are directly dependent on the selected dose criterion. This is illustrated in Figures 1 to 8 by comparing typical discharges by a number of NORM industries with derived screening levels of discharge based on dose criteria of 10, 100 and 300 μSv y^{-1}.

If discharge screening levels are exceeded the actual level of discharges should be verified, discharge conditions (e.g. stack height, river flow) and the existence of assumed exposure pathways should be checked and a decision should be made on the need for site-specific assessment.

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References

Carruthers et al, 1994: D.J. Carruthers, D.R.J. Holroy, J.C.R. Hunt, W.S. Weng, A.G. Robins, D.D. Apsley, D.J. Thomson. and F.B. Smith, “UK-ADMS - a New Approach to Modeling Dispersion in the Earth’s Atmospheric Boundary-Layer”, in Journal of Wind Engineering and Industrial Aerodynamics, Vol. 52, 1994, pp.139-153.

EC, 2003: European Commission, General Directorate Energy and Transport, “MARINA II – Update of the MARINA Project on the radiological exposure of the European Community from radioactivity in North European marine waters”, Radiation Protection Publication RP 132, Vol. 1 and 2, Luxembourg, 2003.

EC, 2004: European Commission, General Directorate Energy and Transport, “Effluent and Dose Control from European Union NORM Industries – Assessment of Current Situation and Proposal for a Harmonised Community Approach”, Radiation Protection Publication RP 135, Vol. 1 and 2, Luxembourg, 2004.

European Council, 1996: “Council Directive 96/29/Euratom of 13 May 1996 laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation”, Official Journal L 159, Luxembourg, 1996.

Lepicard et al, 1998: S. Lepicard, D. Raffestin and F. Rancillac, “Poseidon: A dispersion computer code for assessing radiological impacts in a European sea water environment”, Radiat Prot Dosim, Vol. 75, 1998, pp.79-83.

Mayall et al, 1997: A. Mayall, T. Cabianca, C.A. Attwood, C.A. Fayers, J.G. Smith, J. Penfold, D. Steadman, G. Martin, T.P. Morris and J.R. Simmonds, “PC CREAM 97”, (Code updated in 1998 – PC CREAM 98), EUR 17791 (NRPB-SR296), NRPB, Chilton, 1997.

NCRP, 1996: National Council on Radiation Protection and Measurements, “Screening models for releases of radionuclides to atmosphere, surface water, and ground”, NCRP Report No. 123, 1996.

Ryan et al, 2004a: T.P. Ryan, A. Janssens, E. Henrich, J.L. Daroussin, “New Regulatory Developments and Guidance in the EU with regard to NORM”; This conference, 2004.

Ryan et al, 2004b: T.P. Ryan, A. Janssens, E. Henrich, J.L. Daroussin, Z.K. Hillis, E.I.M. Meijne “Industries Giving Rise to NORM Discharges in the EU – A Review “; This conference, 2004.

Tables

Table 1 Screening levels in GBq y^{-1} for discharges into the atmosphere based on a screening level dose criterion of 300 µSv y^{-1} to critical groups.

Nuclide or chain segment	Stack 10 m	Critical pathway	Stack 50 m	Critical pathway	Stack 100 m	Critical pathway	Stack 200 m	Critical pathway
^{238}U+	1.4E+02	I	2.3E+03	I	1.2E+04	I	2.3E+04	I
^{235}U+	1.2E+02	I	2.2E+03	I	9.3E+03	I	2.0E+04	I
^{234}U	1.1E+02	I	2.0E+03	I	1.0E+04	I	2.0E+04	I
^{232}Th	1.4E+01	I	2.1E+02	I	7.3E+02	E	1.9E+03	I
^{230}Th	2.8E+01	I	5.1E+02	I	2.7E+03	I	5.0E+03	I
^{228}Th+	9.3E+00	I	1.7E+02	I	9.4E+02	I	1.7E+03	I
^{231}Pa+	2.8E+00	I	4.8E+01	I	2.2E+02	I	4.6E+02	I
^{228}Ra+	1.2E+02	I	1.5E+03	C	4.1E+03	C	1.2E+04	C
^{226}Ra+	6.6E+01	I	7.3E+02	C	1.6E+03	E	5.4E+03	E
^{227}Ac+	7.1E-01	I	1.3E+01	I	7.3E+01	I	1.3E+02	I
^{222}Rn	1.5E+05	I	2.7E+06	I	1.6E+07	I	2.8E+07	I
^{220}Rn	2.0E+03	I	3.7E+04	I	2.1E+05	I	3.7E+05	I
^{210}Pb+	1.6E+02	C	1.6E+03	C	3.1E+03	C	1.1E+04	C
^{210}Po	7.0E+01	I	8.0E+02	C	1.7E+03	C	5.8E+03	C

NB I = Plume inhalation, C = Consumption of food and E = External radiation.

Table 2 Screening levels in GBq y^{-1} for discharges into a <u>small river</u> based on a screening level dose criterion of 300 µSv y^{-1}.

Radionuclide or chain segment	Small river			
	Average consumption/ occupancy	**Critical pathway**	**High consumption/ occupancy**	**Critical pathway**
^{238}U	**8.3E+02**	W	5.8E+02	W
^{235}U	7.7E+02	W	5.4E+02	W
^{234}U	**7.7E+02**	W	5.4E+02	W
^{232}Th	**4.8E+03**	E	4.0E+03	E
^{230}Th	**4.3E+03**	E	3.7E+03	E
^{228}Th	**4.9E+00**	E	4.9E+00	E
^{231}Pa	5.9E+01	W	4.2E+01	W
^{228}Ra	**4.2E+01**	W	1.6E+01	F
^{226}Ra	**7.5E+01**	W	3.4E+01	F

^{227}Ac	2.6E+01	W	1.5E+01	F
^{210}Pb	**3.2E+01**	F	5.0E+00	F
^{210}Po	**3.7E+01**	W	1.3E+01	F

NB Results in bold used for comparison with doses from typical discharges. W = water ingestion, F = Fish consumption and E = External radiation.

Table 3 Screening levels in GBq y^{-1} for discharges into a medium river based on a screening level dose criterion of 300 μSv y^{-1}

Radionuclide or chain segment	Medium river			
	Average consumption/occupancy	**Critical pathway**	**High consumption/occupancy**	**Critical pathway**
^{238}U	3.3E+04	W	**2.3E+04**	W
^{235}U	3.1E+04	W	2.2E+04	W
^{234}U	3.1E+04	W	**2.1E+04**	W
^{232}Th	1.9E+05	E	**1.6E+05**	E
^{230}Th	1.7E+05	E	**1.5E+05**	E
^{228}Th	2.0E+02	E	**2.0E+02**	E
^{231}Pa	2.4E+03	W	1.7E+03	W
^{228}Ra	1.7E+03	W	**6.4E+02**	F
^{226}Ra	3.0E+03	W	**1.4E+03**	F
^{227}Ac	1.1E+03	W	6.2E+02	F
^{210}Pb	1.3E+03	F	**2.0E+02**	F
^{210}Po	1.5E+03	W	**5.3E+02**	F

NB Results in bold used for comparison with doses from typical discharges. W = water ingestion, F = Fish consumption and E = External radiation.

Table 4 Screening levels in GBq y^{-1} for discharges into a large river based on a screening level dose criterion of 300 μSv y^{-1}

Radionuclide	Large river			
	Average Consumption and occupancy	**Critical pathway**	**High Consumption and occupancy**	**Critical pathway**
^{238}U	1.6E+05	W	**1.2E+05**	W
^{235}U	1.55E+05	W	1.1E+05	W

^{234}U	1.54E+05	W	**1.1E+05**	W
^{232}Th	9.61E+05	E	**8.1E+05**	E
^{230}Th	8.53E+05	E	**7.4E+05**	E
^{228}Th	9.80E+02	E	**9.8E+02**	E
^{231}Pa	1.19E+04	W	8.5E+03	W
^{228}Ra	8.39E+03	W	**3.2E+03**	F
^{226}Ra	1.51E+04	W	**6.9E+03**	F
^{227}Ac	5.30E+03	W	3.1E+03	F
^{210}Pb	6.35E+03	F	**1.0E+03**	F
^{210}Po	7.42E+03	W	**2.6E+03**	F

NB Results in bold used for comparison with doses from typical discharges. W = water ingestion, F = Fish consumption and E = External radiation.

Table 5 Example calculations showing annual discharges into the sea in GBq y^{-1} that would result in a calculated dose of 300 μSv y^{-1} to critical groups.

Nuclide or chain segment	Small compartment (50 – Baie de la Seine)				Large compartment (59 – North Sea North)			
	Average Consumption and occupancy	Critical pathway	High Consumption and occupancy	Critical pathway	Average Consumption and occupancy	Critical pathway	High Consumption and occupancy	Critical pathway
^{238}U+	8.3E+07	M	9.2E+06	C	7.8E+08	F	8.1E+07	F
^{234}U	1.1E+08	M	1.6E+07	C	4.5E+09	M	6.2E+08	C
^{232}Th	8.3E+04	F	5.4E+03	E	1.8E+07	F	6.6E+05	F
^{230}Th	3.0E+06	F	2.4E+05	F	2.1E+08	F	1.6E+07	F
^{228}Th+	2.2E+06	F	9.3E+04	E	4.9E+08	F	2.0E+07	E
^{228}Ra+	1.0E+05	F	1.2E+04	F	1.1E+07	F	1.1E+06	F
^{226}Ra+	2.2E+05	F	2.2E+04	F	1.0E+07	F	1.0E+06	F
^{210}Pb+	3.3E+05	F	3.0E+04	C	2.3E+07	C	1.5E+06	C
^{210}Po	1.4E+06	C	8.9E+04	C	7.4E+07	C	4.8E+06	C

NB M = Molluscs consumption; F = Fish consumption; C = Crustacea consumption; E = external radiation.

Figures

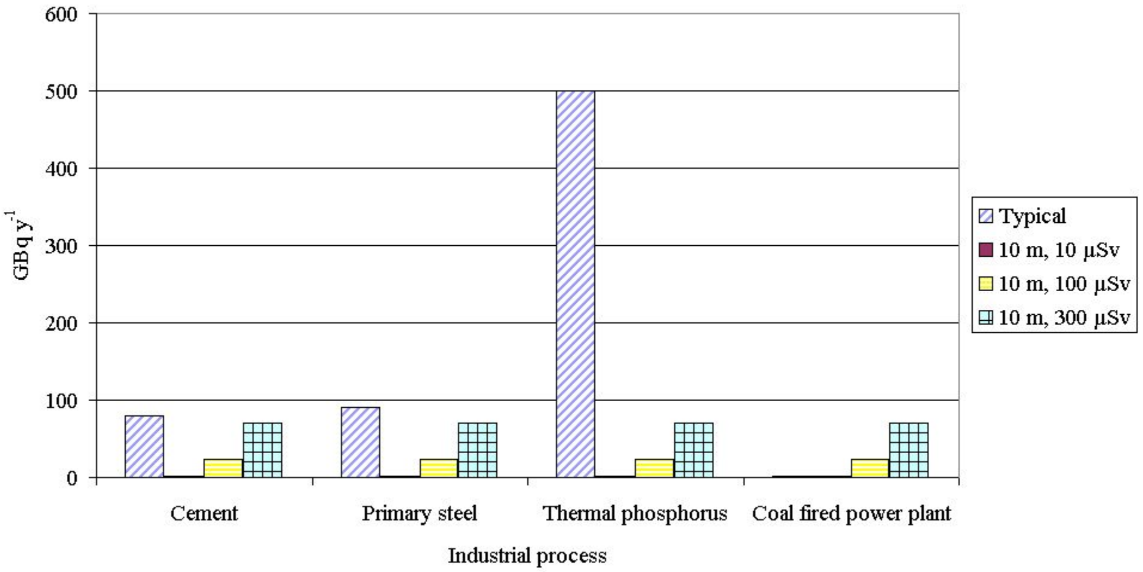

Figure 1 Comparison of typical aerial discharges of ^{210}Po with derived screening levels for a 10 m stack height using three different dose criteria

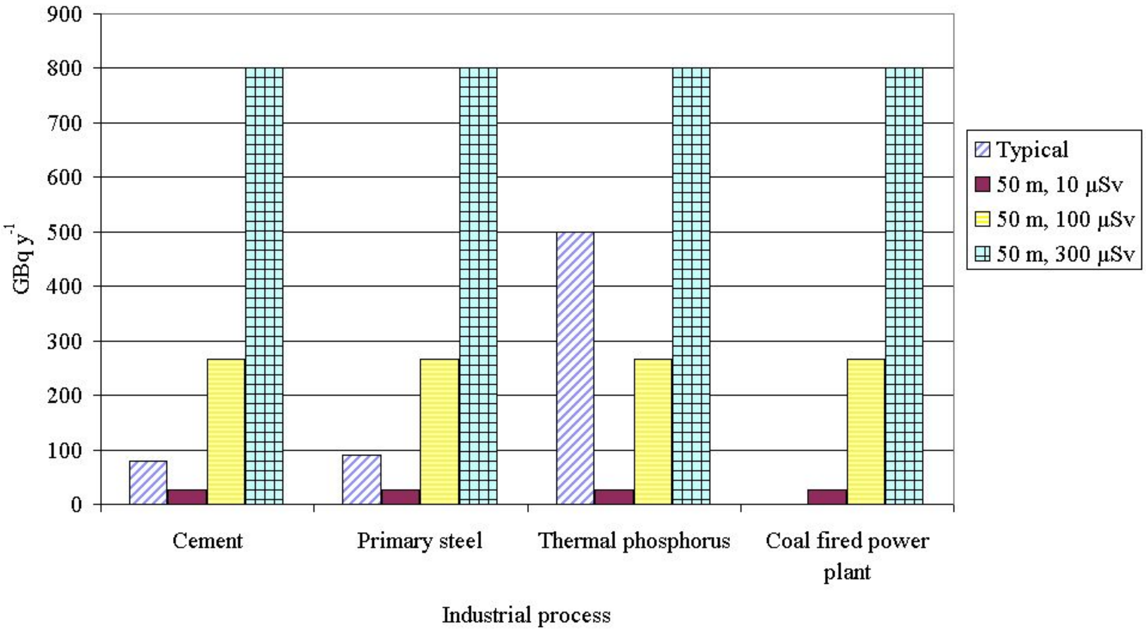

Figure 2 **Comparison of typical aerial discharges of ^{210}Po with derived screening levels for a <u>50 m stack</u> height using three different dose criteria**

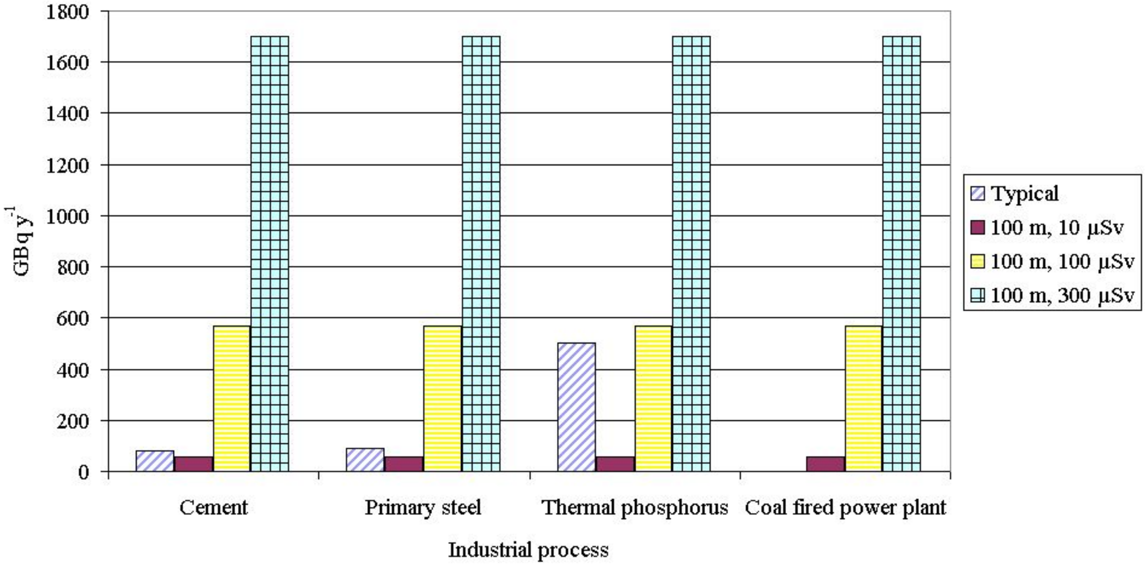

Figure 3 Comparison of typical aerial discharges of ^{210}Po with derived screening levels for 100 m stack height using three different dose criteria

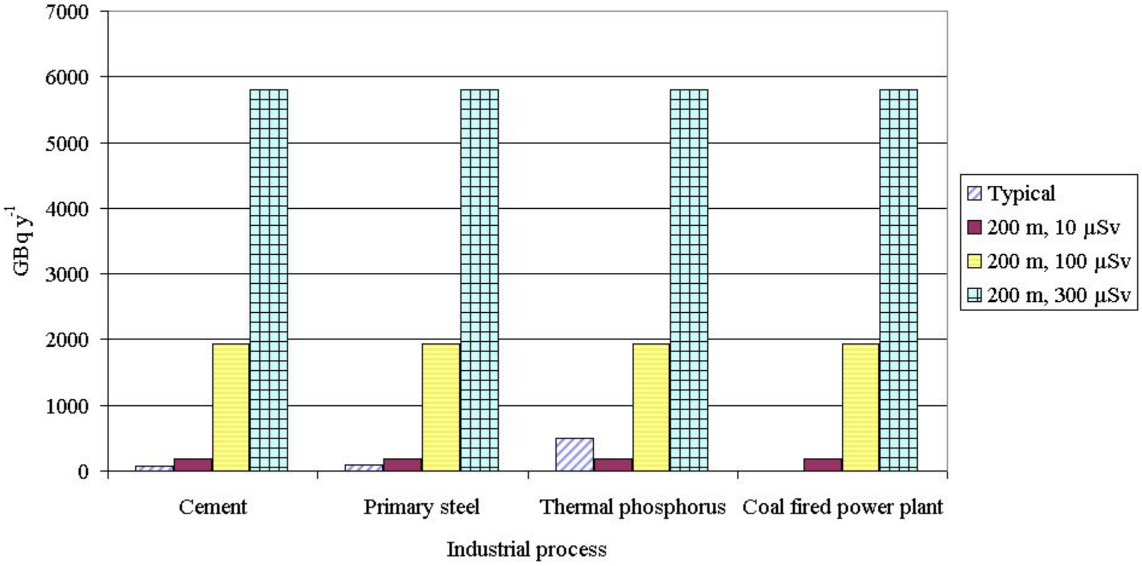

Figure 4 Comparison of typical aerial discharges of ^{210}Po with derived screening levels for 200 m stack height using three different dose criteria

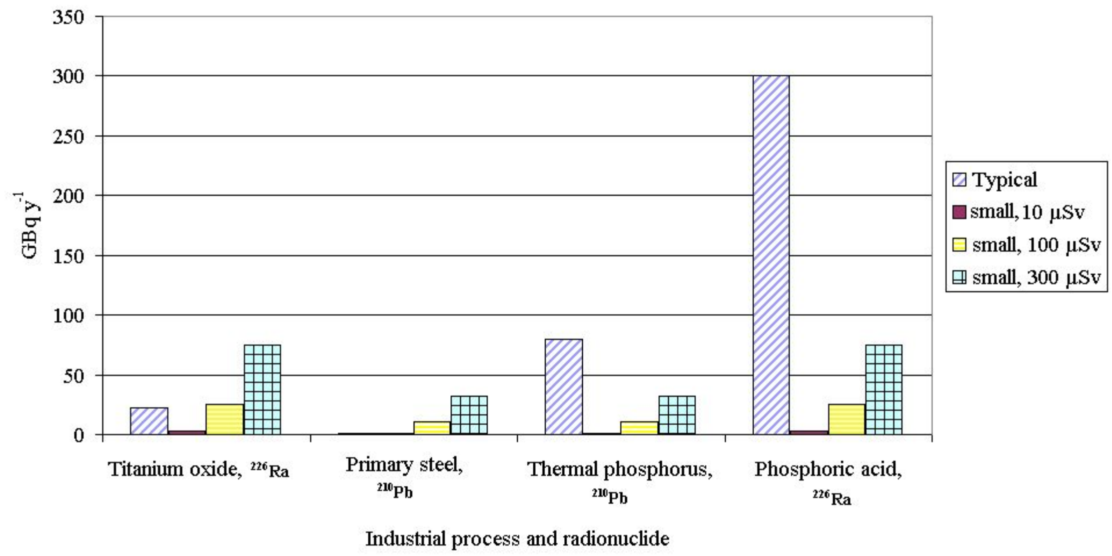

Figure 5 **Comparison of typical discharges with derived screening levels for a small river using three different dose criteria**

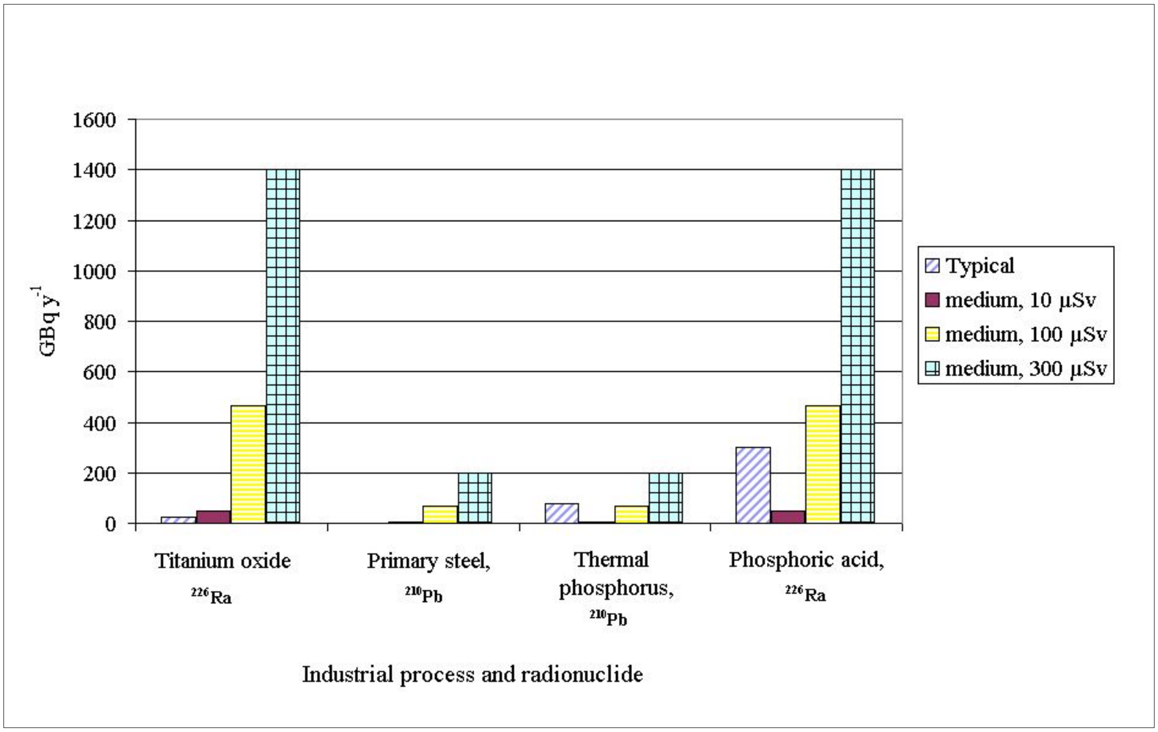

Figure 6 Comparison of typical discharges with derived screening levels for a medium river using three different dose criteria

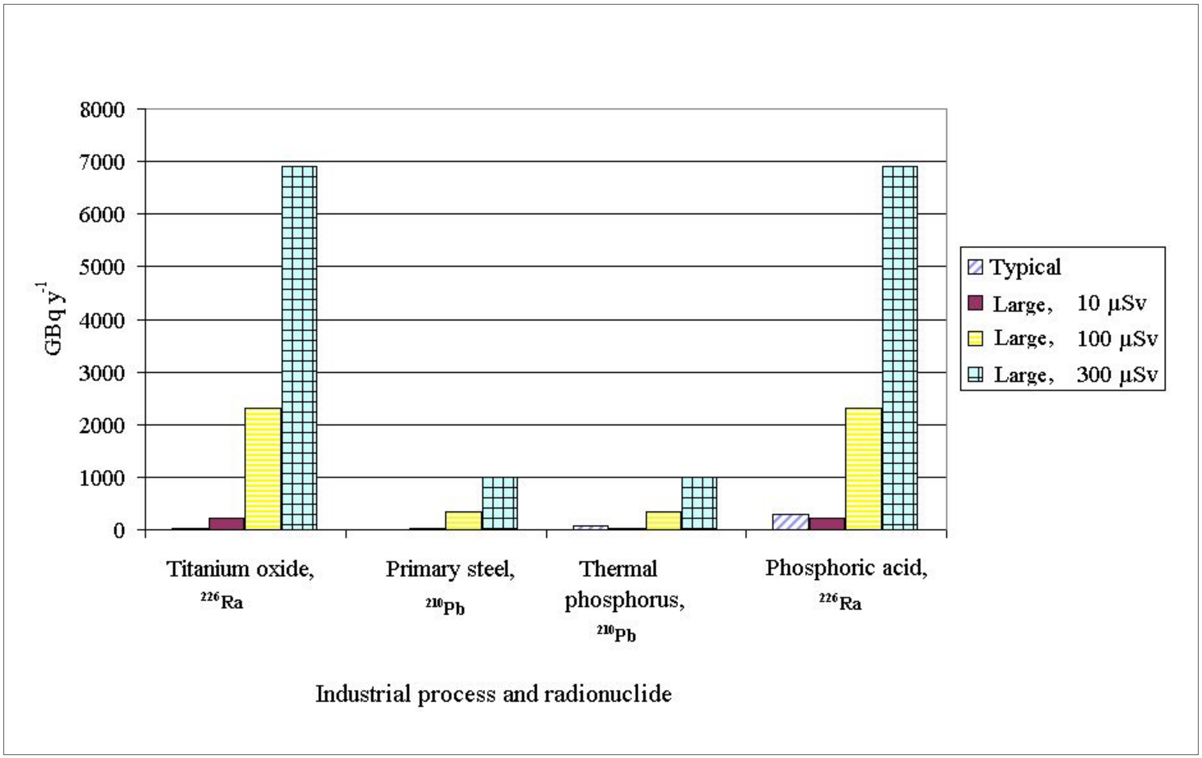

Figure 7 Comparison of typical discharges with derived screening levels for a large river using three different dose criteria

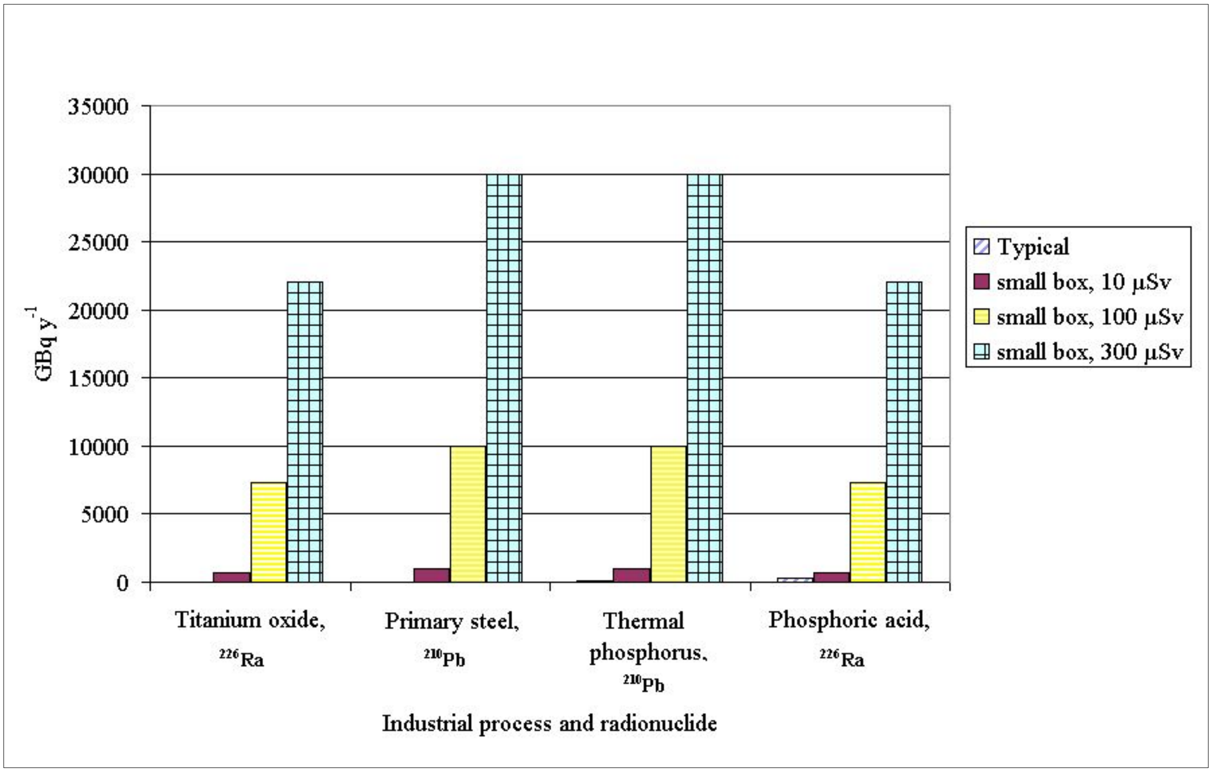

Figure 8 Comparison of typical discharges with the calculated discharges in a small marine box resulting in three levels of dose being reached

POLISH NATIONAL INTERCALIBRATIONS OF MEASUREMENT METHODS OF ^{222}RN CONCENTRATION IN WATERS

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ABSTRACT

The paper presents the results of intercalibration measurements of ^{222}Rn concentration in water samples. In total, 11 laboratories from many Polish research and commercial institutions took part in the abovementioned measurements. Seven of them participated in 3 intercalibration measurements organized in the years 2001 – 2003. In 2001 and 2002, the intercalibration measurements were carried out in the Sudety Mountains (Szczawno Zdrój and Świeradów Zdrój health-resorts respectively). During these two experiments water samples were taken from mineral springs, considered medicinal in Poland. They are characterized by an increased CO_2 concentration (0.53 – 2.54 g/dm^3), as well as different values of total dissolved solids

(TDS between 0.15 and 3.82 g/dm^3), and radon concentration (between 10 and 1170 Bq/dm^3), and other distinct differences in chemical composition and physical properties. In 2003, experiment measurements were carried out in water samples prepared in CLOR laboratory in Warsaw. The samples were produced by the aeration of a 10-dm^3 container filled with tap water with air enriched by ^{222}Rn coming from a PYLON source (502.5 kBq activity of ^{226}Ra). During all intercalibration experiments, the concentration of ^{222}Rn in 7 water samples (2, 3 and 2 in 2001, 2002 and 2003 respectively) was determined. Special care was taken to ensure the same conditions of collecting water samples for each participant.

The laboratories participating in the experiments applied different techniques to determine the concentration of ^{222}Rn in the water samples: a liquid scintillation method, gamma detectors, Lucas cells and ionisation chambers.

The obtained results confirmed that keeping the containers with water samples closed tightly from the moment of collecting till the measurement was of great importance. It happened twice, in different laboratories, that a leakage in the measurement set-up (in the AlphaGUARD™ + AquaKIT™ system) resulted in getting underrated values of ^{222}Rn concentrations. The best consistency of the results in all 3 intercalibration measurements was obtained by the laboratories using the liquid scintillation method. It has been observed, that the number of laboratories that got consistent results (within error limits) increased from about 50% in 2001 to nearly 100% in 2003. This confirms the fact that the organised experiments meet the main task – improving the correctness of the results obtained in particular laboratories. Thus, it seems necessary to organise such experiments in the next years.

The intercalibrations in 2002 and 2003 were organized within the activities of the Radon Centre and with its financial support.

INTRODUCTION

In the years 2001 – 2003, 3 national intercalibrations of methods used for measuring radon (^{222}Rn) concentrations in water samples were organised in Poland. Twice, in 2001 and 2002, they were organized by Wrocław University of Technology, and the 2003 comparative experiment was organised by the Central Laboratory for Radiological Protection in Warsaw. The comparative experiments in 2002 and 2003 were carried out within the activities of the Radon Centre – an international non-government scientific network, and in 2003 they were also financed by this organisation. In 2001 and 2002, the determination results of ^{222}Rn concentrations dissolved in natural groundwaters flowing out in the Sudetes (in Szczawno Zdrój in 2001, and in Świeradów Zdrój in 2002) were compared (Fig. 1). In 2003, water samples for comparative measurements were prepared in a laboratory.

The overall number of 11 laboratories from different Polish scientific institutes and commercial organizations dealing with measurements of radon concentrations in waters took part in the comparative experiments. Seven of them participated in all the three comparative experiments.

WATER SAMPLES

In 2001, intercalibration measurements were based on samples of groundwaters flowing out of two springs (“Marta” and “Mieszko”) in Szczawno Zdrój (cf. Fig. 1). The waters from “Mieszko” spring are waters type HCO_3–Na, with temperature oscillating between 7.3 and 13.1ºC. The value of total dissolved solids (TDS) varies from 2.34 to 3.82 g/dm^3. The waters are also characterised by a high concentration of dissolved CO_2, oscillating between 0.81 and 2.24 g/dm^3. The concentration of ^{222}Rn in the waters from this spring varies from 10.4 to 55.1 Bq/dm^3, with the arithmetic mean value of 30.3 Bq/dm^3 for 26 measurements conducted in the years 1974 – 1998. The spring discharge is not big and varies from 0.16 to 0.51 m^3/h. The waters from “Marta” spring belong to the type HCO_3–Na–Ca. Their TDS values oscillate between 1.13 – 2.70 g/dm^3, the temperature reaches 8.3 – 14.3ºC, and the content of CO_2 oscillates between 1.23 and 2.15 g/dm^3. The concentration of ^{222}Rn dissolved in the waters from “Marta” spring varies from 103.6 to 325.6 Bq/dm^3, with the arithmetic mean value of 214.1 Bq/dm^3 for 860 measurements conducted in the years 1974 – 1998. The spring discharge is very low and fluctuates from 0.016 to 0.07 m^3/h (Przylibski et al., 2001).

In 2002, groundwater samples for comparative measurements were taken from three wells in “Górne” intake in Świeradów Zdrój (cf. Fig. 1). In these wells, waters type HCO_3-Ca-Mg are extracted, with the total self-outflow discharge varying between 0.11 and 1.86 m^3/h. The water temperature oscillates in time between 8 and 16ºC and is similar in all the wells situated in the cellar of the Spa House. TDS values change in time from 0.15 to 0.63 g/dm^3 and are comparable in all the three wells, just as the concentrations of the dissolved carbon dioxide, whose values change in time from 0.53 to 2.54 g/dm^3. The concentration of ^{222}Rn in the waters of particular wells ranges between 155 and 614 Bq/dm^3 with the average of 336 Bq/dm^3 for 27 data, between 81 and 1145 Bq/dm^3 with the average of 210 Bq/dm^3 for 27 data, and between 37 and 1170 Bq/dm^3 with the average of 510 Bq/dm^3 for 1953 data in wells 1, 2 and 3 respectively. The measurements were conducted in the years 1986 – 2002 (Przylibski, in press).

In 2003, in the Central Laboratory of Radiological Protection in Warsaw, two 10-litre bottles with a faucet near the bottom were prepared and filled with tap water. The radon produced in the flow through a radon source of the activity of 502.5 kBq manufactured by Pylon™ was used to saturate the water in both bottles. In order to get a radon concentration of ca. 500 Bq/dm^3 on the day of the intercalibration exercise, the full production of radon from the source (closed 30 days earlier) was pumped through a plastic hose to the volume of water in one bottle. The pumping with the flow rate of 0.05 dm^3/min. lasted 80 minutes. Next, the water waited 7 days to be sampled for intercalibration. The water with low radon concentration of ca. 30 Bq/dm^3 was prepared directly before sampling. First, the radon source was unloaded of radon and only the running production of radon was pumped into the water during one hour, with the flow rate of 0.05 dm^3/min. It was observed that while using the flow rate of 0.05 dm^3/min., ca. 5 – 6% of the pumped-in radon was dissolved in the water.

Jointly, in all the experiments, ^{222}Rn concentration values measured in 7 water samples were compared: 2 in 2001, 3 in 2002 and 2 in 2003.

MEASUREMENT METHODS

The organizers of individual experiments paid particular attention to ensuring all the participants identical conditions of taking water samples of whatever volume (according to the requirements of each of the applied measurement methods). This concerned chiefly minimizing the time of taking samples by all the participants. The time usually did not exceed 20 minutes for one intake or one sample for all the participants altogether. This was especially important in the case of taking groundwater samples. After the moment of sample taking, each laboratory followed its own measurement procedure, paying special attention to a fast transfer to the laboratory and ensuring the impermeability of the container with the water sample.

Particular laboratories used different methods to determine the concentration of ^{222}Rn in the taken water samples.

METHOD no. 1

5 out of 11 laboratories participating in the intercalibration measurements of ^{222}Rn concentration applied the liquid scintillation technique (laboratories 1, 2, 3, 5, 11). The procedure for radon determination by liquid scintillation counting is fast and simple. A sample of 10 ml of water is drawn by a disposable syringe and immediately transferred into a vial containing 10 ml of liquid scintillator solution. The vial is capped, shaken and taken to the laboratory for measurement. Radon will permeate from the water phase to the organic scintillant solution phase. The alpha activity of ^{222}Rn and its decay products is measured with the liquid scintillation counter (Wallac™, Quantulus™, TRI-CARB™).

METHOD no. 2

2 laboratories measured radon concentration in water using the professional radon monitor AlphaGuard™ (laboratories 4, 7). This is an ionisation chamber, designed for measuring radon in air, soil and water. For measuring ^{222}Rn concentration in water, additional equipment AquaKIT™ is used. In a closed gas cycle, radon is extracted from a water sample (placed in a degassing vessel) by means of a pump. The security vessel is connected with the degassing vessel. All drops are deposited in it if they get into the gas cycle during the degassing process. By doing this, the stress of the water vapour is minimised for the radon monitor. Radon concentration in this system was determined with the AlphaGuard™, whose ionisation chamber is also part of the gas cycle.

METHOD no. 3

A detector with a Lucas cell was used in laboratory 9 for detecting and measuring radon in water samples. The detector consists of a Lucas cell coupled to a photomultiplier tube. The inside walls of Lucas cells are covered with a scintillator of activated zinc sulphide (ZnS(Ag)), which responds to alpha radiation from radon decay, but is insensitive to beta and gamma. Air, flowing through the investigated water, washes away the radon contained in it. After reaching the equilibrium state between radon and its daughters, the container with air is placed in the Lucas cell. When decaying, radon and its daughters emit alpha particles that hit the zinc sulphide within the cell. The alpha particle interacting with the scintillator produces a pulse of light that is converted into an electric pulse by the photomultiplier tube. The electric pulses are amplified and counted. The light output is proportional to alpha-ray energy.

METHOD no. 4

An electrometer SG-11 determines the content of ^{222}Rn in water samples in laboratory 8. The electrometer measures the ion current produced by the radioactivity of radon in the ionisation chamber. The radon enters the chamber from the water sample by blowing some air through the measured sample. The electrometer is mounted on the microscope stage so that the electrometer fibre can be viewed through the lens. A scale inserted in the microscope eyepiece permits a quantitative measurement of the fibre’s deflection during the observation period. The velocity of the fibre’s deflection is a measure of the concentration of ^{222}Rn in the ionisation chamber.

METHOD no. 5

In laboratory 6, special equipment is used for measuring radon in water. The main part of this detection device is a scintillation chamber in the shape of a 6-dm^3 tube.

The tube contains 2 photomultiplier tubes that work concurrently. The collecting electrode is covered with a scintillator of activated ZnS(Ag). The alpha radiation from ^{222}Rn and its daughters is converted into light that, in turn, is converted into electric pulses that are amplified and counted. The measurements are made after 180 minutes (in the equilibrium state).

METHOD no. 6

The measurement of ^{222}Rn concentration in laboratory 10 was performed by a NaI scintillation detector SSU-70™. The scintillation detector collecting gamma radiation is connected with an electronic system. The window of a single-channel analyser is set on a gamma line of ^{214}Bi, a short-lived decay product of ^{222}Rn. The measurements are made after 4 hours, when the equilibrium state between ^{214}Rn and ^{222}Rn is achieved. The scintillation detector is sunk inside an open vessel containing a 1-dm^{3} water sample. The content of ^{222}Rn in this sample corresponds to the counting rate in the counter.

RESULTS AND DISCUSSION

In the first two comparative experiments, ^{222}Rn concentration in the investigated waters was unknown, except for the range of values measured during the last few decades. Therefore, it was impossible to determine the concentration to which the obtained results should be referred. Consequently, the comparative measurements of radon concentrations in groundwaters were aimed chiefly at checking the consistency of the results obtained by particular laboratories. An important element of the comparative measurement was examining the influence of the increased content of carbon dioxide dissolved in these waters, as well as an increased TDS value in some intakes, on the quality of the obtained results.

During the first comparative experiment, ^{222}Rn concentrations were measured in water samples from “Marta” and “Mieszko” intakes in Szczawno Zdrój. The results obtained by particular laboratories have been presented in Fig. 2 and 3. The results from laboratories 1 – 6 were regarded as reliable for the water samples from “Marta” intake. All of them were comparable within error limits. These laboratories included all those using the liquid-scintillation technique. The results obtained by the remaining laboratories are much underrated, which is probably related to the degassing of the samples before or during the measurement, or even during the sample-taking. In laboratory 7, a leakage in the measurement circuit was detected after the experiment, which could verify the above interpretation. It is difficult to interpret the results obtained for the samples from “Mieszko” intake without a reference value. The only obvious thing is the underrated value obtained in laboratory 7 due to the discovered leakage in the measurement circuit. The higher results obtained by laboratories 1, 2, 5 and 6 seem more probable. It is also possible that the conditions of sample-taking had changed during the process, resulting in the lowering of radon concentration in the water taken for the experiment. Hence, it should be accepted that four out of the nine laboratories participating in the intercalibration measurements got satisfactory results, and other 2 obtained good results for one sample.

In view of the inconsistency of the results produced in the first comparative experiment, and a large number of laboratories which obtained unsatisfactory results, another experiment was organised. This time, samples were taken from three wells of “Górne” intake in Świeradów Zdrój. The results obtained by particular laboratories have been presented in Figs. 4, 5 and 6. Again, a leakage was found in a measurement set, this time in laboratory 4, which resulted in considerable underrating of measurement results for all samples. In the water samples from well no. 1, only four laboratories (no. 2, 3, 5, and 7) got results comparable within error limit. The results obtained by the remaining laboratories should be considered underrated. In the water samples from wells no. 2 and 3, the results obtained by laboratories no. 1, 2, 3, 5, and 7 were comparable within error limit, and simultaneously the highest, and they should be considered accurate. These laboratories include all of those which apply liquid-scintillation technique. Thus, among nine laboratories participating in the 2002 comparative experiment, five obtained satisfactory results, including four which had also obtained satisfactory or good results in 2001. These are the laboratories using liquid-scintillation technique.

The latest experiment, carried out in 2003 in the Central Laboratory of Radiological Protection in Warsaw, used waters prepared in the way enabling an estimation of a reference value to be compared with the results obtained by particular laboratories. The measurement results for two samples with radon concentrations of c. 500 and c. 30 Bq/dm^3 have been presented in Figs. 7 and 8. For the sample with the higher radon concentration, 7 out of 8 laboratories participating in the experiment obtained results comparable within measurement error limit, hence satisfactory. At the same time, they were slightly (about 10%) lower than the estimated reference value. As for the water sample with the lower ^{222}Rn concentration, all laboratories obtained results comparable within measurement error limit and about 10% lower than the estimated reference value, i.e. satisfactory. Also in this comparative experiment, very good results were obtained by the laboratories using liquid-scintillation technique. Equally good results were obtained in the laboratories using AquaKIT™ set and AlphaGUARD™ monitor equipped with an ionisation chamber.

CONCLUSIONS

Organizing successive comparative experiments of ^{222}Rn concentrations in groundwaters brought about the expected effect, which is the obtaining of more and more convergent results by all laboratories. In the 2001 intercalibration measurements, hardly 50% of the participating laboratories produced satisfactory results, while in 2003 practically all laboratories measured radon concentrations comparable within error limit and close to the estimated reference value. The results of the subsequent intercalibration experiments proved that a very good method of measuring ^{222}Rn concentrations in these waters, including groundwaters, is the liquid-scintillation technique. Equally good results were obtained using an ionisation chamber to measure radon previously extracted to a gas phase.

In view of indisputable benefits to all laboratories measuring ^{222}Rn concentrations in waters for human consumption, waters regarded as medicinal, groundwaters and surface waters used for geochemical and other research, next experiments of this kind are planned in the following years within the activities of the Radon Centre – a non-government international scientific network. Slightly worse results of the experiments based on groundwater samples suggest that future intercalibration measurements should include both natural waters and laboratory-prepared waters with the defined reference concentration of radon.

ACKNOWLEDGEMENTS

The authors would like to thank the following people for enabling them to take samples of medicinal groundwaters in the health resorts Szczawno Zdrój and Świeradów Zdrój and for the extensive help during their stay in the resorts: Ms Teresa Dragunowicz from the Resort Mining Institute in the resort Świeradów-Czerniawa Sp. z o.o., and Mr Paweł Filbier from the Resort Mining Institute in the resort Szczawno-Jedlina S.A.

REFERENCES

Przylibski T. A., in press – Radon. The specific component of medicinal waters in the Sudety Mountains.

Przylibski T. A., Mroczkowski K., Żebrowski A., Filbier P., 2001 – Radon-222 in medicinal groundwaters of Szczawno Zdrój (Sudety Mountains, SW Poland). Environmental Geology, Vol. 40, No. 4/5, pp. 429-439.

FIGURE CAPTIONS

Fig. 1. Sites of the comparative experiments in the Sudetes on the background of an outline map of Poland: 1 – Szczawno Zdrój, 2 – Świeradów Zdrój.

Fig. 2. Measurement results of ^{222}Rn concentrations in the water sample from "Marta" intake in Szczawno Zdrój obtained by particular laboratories participating in the experiment.

The dotted line indicates the mean arithmetic value of the measurements conducted in 1974 – 1998; the solid lines represent the mean arithmetic value of the highest results and those comparable within measurement error limits obtained by particular laboratories (Labs. 1 – 6), and the doubled value of the standard deviation from that mean.

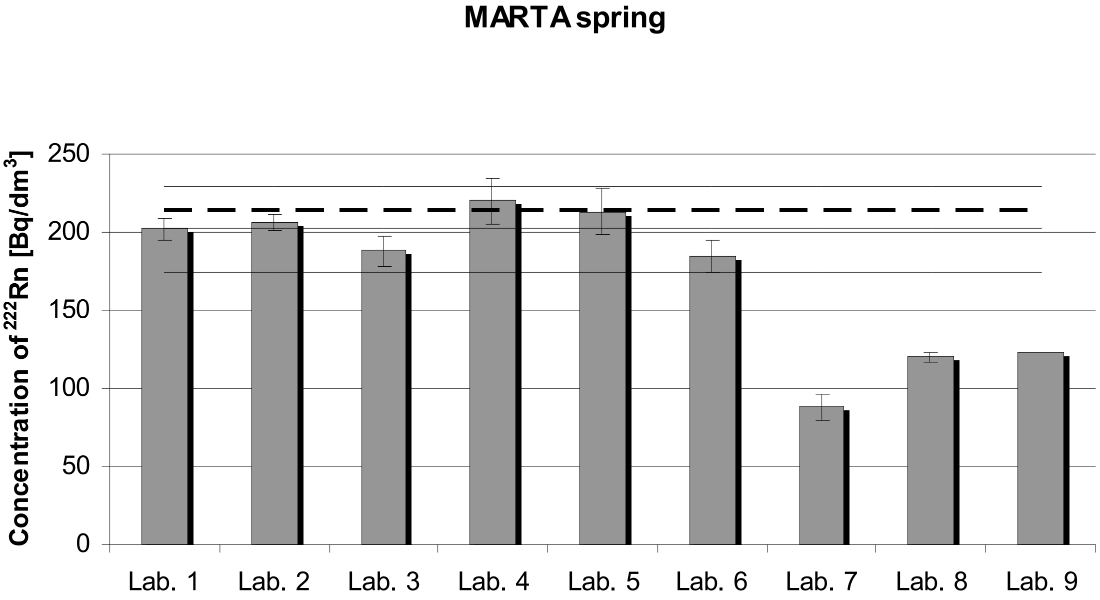


Fig. 3. Measurement results of ^{222}Rn concentrations in a water sample from "Mieszko" intake in Szczawno Zdrój obtained by particular laboratories participating in the experiment.

The dotted line indicates the mean arithmetic value of the measurements conducted in 1974 – 1998; the solid lines represent the mean arithmetic value of the highest results and those comparable within measurement error limits obtained by particular laboratories (Labs. 1, 2, 5 and 6), and the doubled value of the standard deviation from that mean.

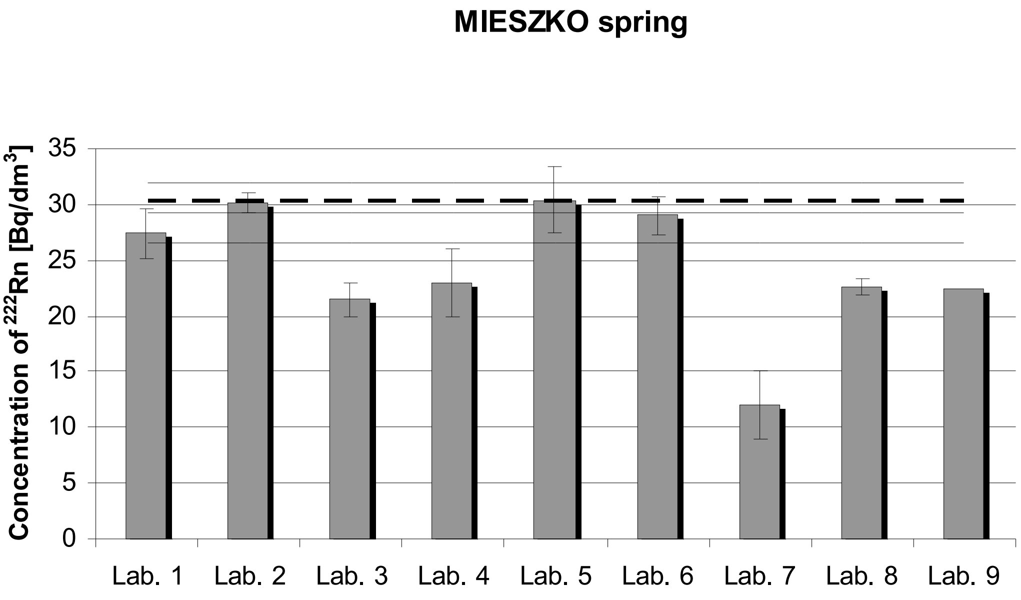


Fig. 4. Measurement results of ^{222}Rn concentrations in a water sample from "Górne" intake (well no. 1) in Świeradów Zdrój obtained by particular laboratories participating in the experiment.

The dotted line indicates the mean arithmetic value of the measurements conducted in 1986 – 2002; the solid lines represent the mean arithmetic value of the highest results and those comparable within measurement error limits obtained by particular laboratories (Labs. 2, 3, 5 and 7), and the doubled value of the standard deviation from that mean.

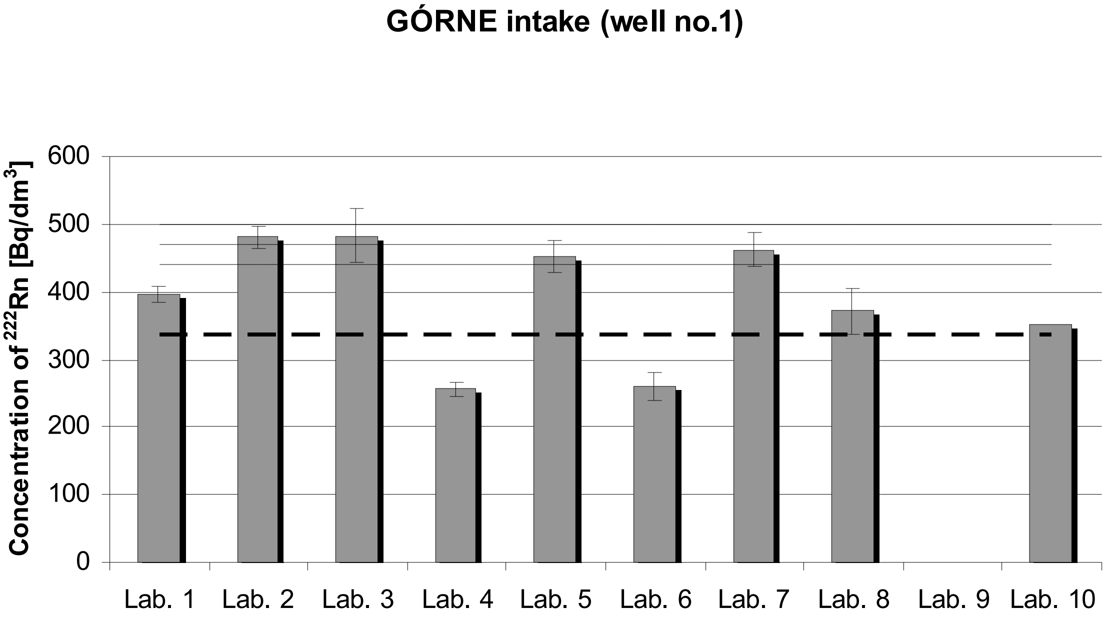


Fig. 5. Measurement results of ^{222}Rn concentrations in a water sample from "Górne" intake (well no. 2) in Świeradów Zdrój obtained by particular laboratories participating in the experiment.

The dotted line indicates the mean arithmetic value of the measurements conducted in 1986 – 2002; the solid lines represent the mean arithmetic value of the highest results and those comparable within measurement error limits obtained by particular laboratories (Labs. 1, 2, 3, 5 and 7), and the doubled value of the standard deviation from that mean.

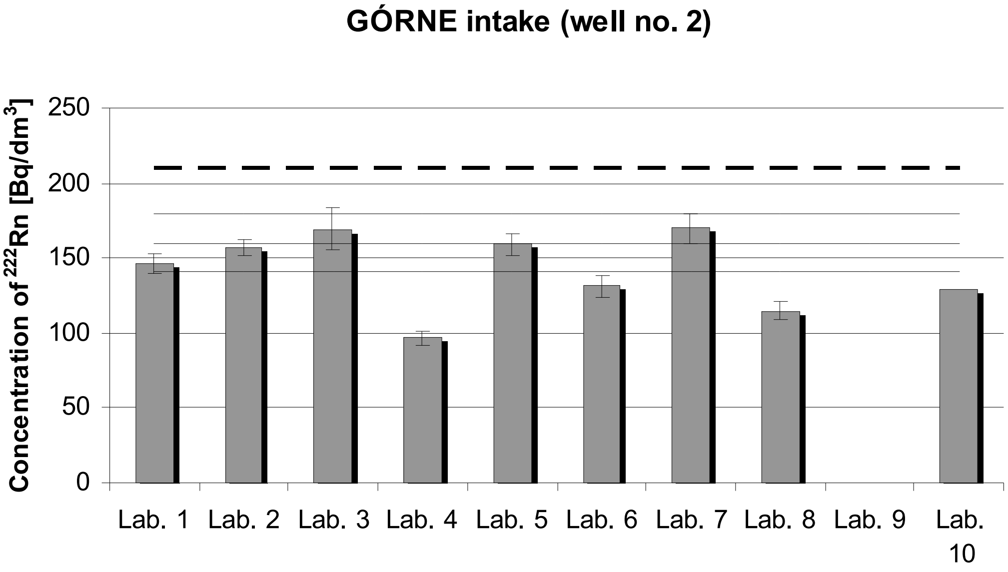


Fig. 6. Measurement results of ^{222}Rn concentrations in a water sample from "Górne" intake (well no. 3) in Świeradów Zdrój obtained by particular laboratories participating in the experiment.

The dotted line indicates the mean arithmetic value of the measurements conducted in 1986 – 2002; the solid lines represent the mean arithmetic value of the highest results and those comparable within measurement error limits obtained by particular laboratories (Labs. 1, 2, 3, 5 and 7), and the doubled value of the standard deviation from that mean.

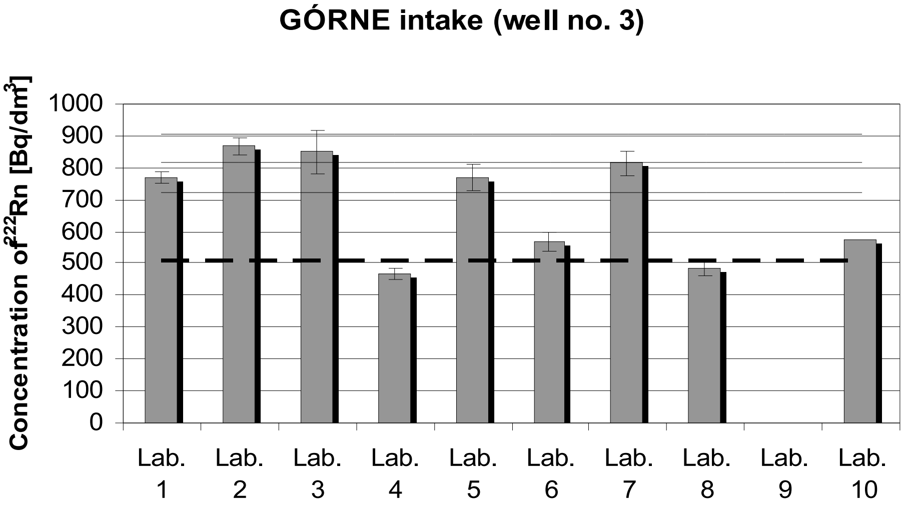


Fig. 7. Measurement results of ^{222}Rn concentrations in a higher concentration water sample (no. 1) prepared in the Central Laboratory of Radiological Protection in Warsaw obtained by particular laboratories participating in the experiment.

The dotted line indicates the estimated value of radon concentration in the prepared water sample; the solid lines represent the mean arithmetic value of the highest results and those comparable within measurement error limits obtained by particular laboratories (Labs. 1, 2, 3, 4, 5, 7 and 11), and the doubled value of the standard deviation from that mean.

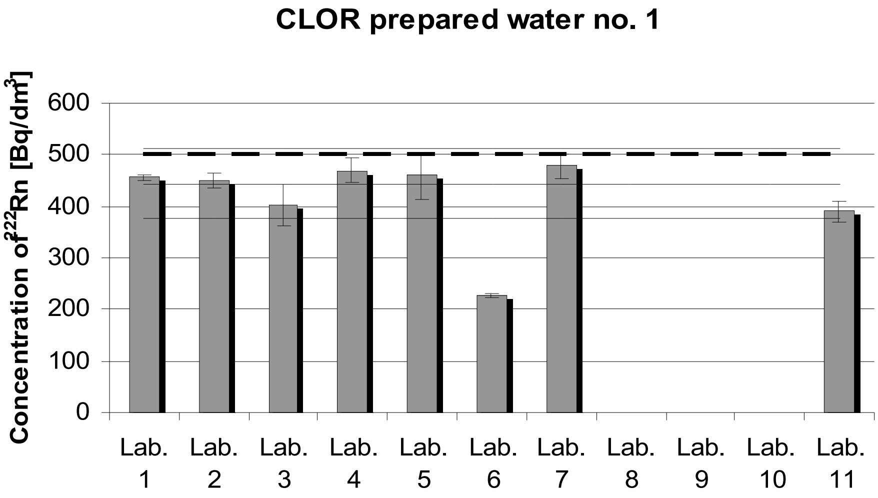
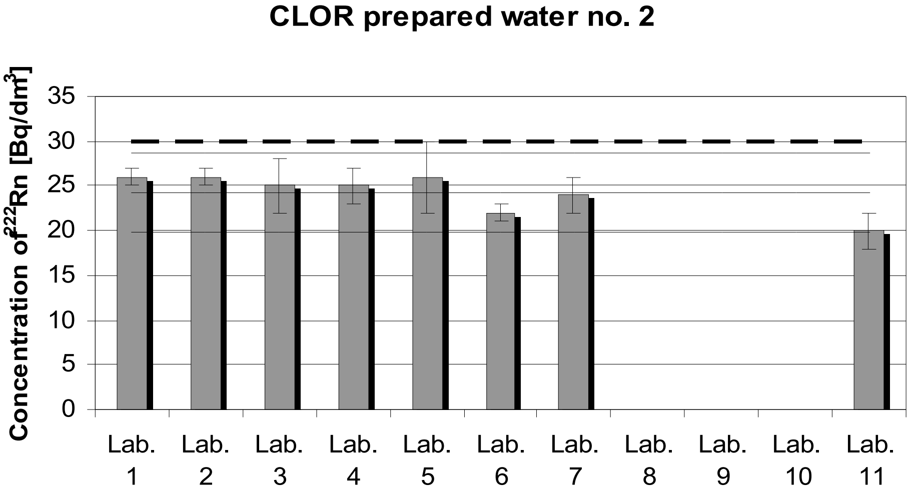


Fig. 8. Measurement results of ^{222}Rn concentrations in a lower concentration water sample (no. 2) prepared in the Central Laboratory of Radiological Protection in Warsaw obtained by particular laboratories participating in the experiment.

The dotted line indicates the estimated value of radon concentration in the prepared water sample; the solid lines represent the mean arithmetic value of the highest results and those comparable within measurement error limits obtained by particular laboratories (all laboratories), and the doubled value of the standard deviation from that mean.



APPLICATION OF INTERNATIONAL SAFETY STANDARDS TO WORK INVOLVING EXPOSURE TO NATURAL RADIATION

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Abstract

The International Basic Safety Standards (BSS), published by the International Atomic Energy Agency (IAEA) in 1996, provide the basis for the control of exposure to both artificial and natural sources of radiation. The IAEA is engaged in a programme to provide additional guidance and information on the application of the BSS to natural sources, and this programme is focusing increasingly on work

activities involving naturally occurring radioactive material (NORM). This paper describes the current status of this programme and, in particular, the progress being made in the development of guidance and supporting information to help national authorities to decide which NORM activities should be regulated and how they should be regulated. Data on activity concentrations, radiation doses and appropriate control measures for various industrial processes involving NORM are being gathered as part of the development of sector-specific Safety Reports and associated training packages. Some examples are given to illustrate how these data provide support for a growing international consensus on criteria for defining the scope of regulatory control and on the need for, and the nature of, a graded approach to regulation.

1. THE IAEA SAFETY STANDARDS

The International Atomic Energy Agency (IAEA) is specifically authorized under the terms of its Statute to establish standards of radiation protection and safety in consultation and, where appropriate, in collaboration with the competent organs of the United Nations and with the specialized agencies concerned, and to provide for the application of these standards. The International Basic Safety Standards (BSS), published by the IAEA in 1996 [1], are jointly sponsored by the IAEA and five other international organizations, and are based on the most recent recommendations of the ICRP [2]. A Safety Guide on Occupational Radiation Protection [3], jointly sponsored by the IAEA and the International Labour Office and published in 1999, provides more detailed guidance on the application of the BSS to natural sources of radiation, including radon and thoron progeny. As part of its safety standards programme over the past 30–40 years, the IAEA has published various safety-related documents dealing with protection against exposure to natural sources of radiation, several of which were jointly sponsored by the IAEA and the International Labour Organization (and some also by the World Health Organization), but these have been concerned primarily with the mining and processing of uranium and thorium ores (see Refs [4–7] for publications still current). Only recently has the coverage been extended more explicitly to other activities that involve exposure to natural sources [8–10].

2. RECENT EVENTS IN THE DEVELOPMENT OF THE IAEA'S PROGRAMME ON EXPOSURE TO NATURAL RADIATION SOURCES

In 1998, it was concluded from an international conference on *Topical Issues in Nuclear, Radiation and Radioactive Waste Safety* [11] that further practical guidance was needed on the control of exposure to natural radiation, in particular, exposure arising from work with material containing elevated levels of natural radionuclides. Such material has come to be referred to as 'naturally occurring radioactive material' (NORM). In 2001, the IAEA held two meetings on *Assessment of Occupational Protection Conditions in Workplaces with High Levels of Exposure to Natural Radiation* to identify more precisely which industries were primarily affected and which industrial processes and materials required control as a priority. From the inputs of the 16 participating countries, it was concluded that the IAEA, in broad consultation with regulatory and advisory bodies and NORM industries, should develop Safety Reports for individual industry sectors in which the control of exposure to NORM needed to be considered. The development of a Safety Report on the oil and gas sector [9] had already been started. The other industry sectors identified included phosphates and phosphoric acid production, zircon sand and zirconia production, titanium dioxide pigment production, monazite and rare earths extraction, industrial uses of thorium, coal and coal ash, and the production of certain metals. It was also recommended that these Safety Reports should be followed up with information exchange and training courses aimed at regulatory bodies, industry personnel and service providers, and supplemented by more general assistance in identifying work activities with significant exposures to NORM and in formulating practical approaches to the assessment and control of those exposures.

In 2002, the IAEA and the International Labour Organization jointly convened in Geneva an international conference on *Occupational Radiation Protection*. One of the issues addressed was occupational exposure to NORM, and the conclusions and recommendations from this conference [12] provided further important input to the consolidation of the IAEA's programme on protection against natural radiation, the key elements of which were (a) to complete the development of supporting documents forming part of the relevant safety standards, (b) to provide for the application of these standards through the fostering of information exchange and promoting research and development, and (c) to support the provision of technical cooperation with Member States. The conference found that, while exposures to NORM were generally stable and predictable, with little or no likelihood of large accidental exposures, lack of suitable controls could in some cases give rise to doses approaching or even exceeding dose limits — these were the situations on which regulatory attention needed to be focused. At the other end of the scale, it was widely believed that, in terms of an optimized approach to protection, occupational doses below 1–2 mSv per year were unlikely to warrant significant regulatory attention and that it would be wasteful of resources, including those of the regulator, to seek further reductions. The conference therefore concluded that more explicit guidance was needed on determining which exposures arising from NORM activities should be subject to some form of regulatory control. For those exposures that did require control, the conference also highlighted the need for guidance on how to apply a graded regulatory approach that was sufficiently flexible and practicable to cater for the full diversity of exposure situations.

3. WHAT SHOULD BE REGULATED?

The question of what should be regulated can be addressed in two basic ways — by specifying either what is outside of the system of control or what is inside the system of control. The BSS make provision for both approaches, as well as for further options within each approach:

- With regard to what is outside the system of control, the BSS provide for exclusion of exposures (from the scope of application of the BSS) or exemption of practices or sources within practices (from requirements of the BSS).
- With regard to what is inside the system of control, the BSS state that certain exposures to natural sources should be automatically included, and identifies these either by specifying the practices and sources giving rise to these exposures or by specifying the exposures themselves. The BSS also make provision for the regulatory body to specify additional practices, sources and exposures that should be included.
- Exposures to natural sources not specifically excluded or included (either automatically or by regulatory decision) are considered as chronic exposure situations. Although these exposure situations are not subject to regulation as practices, some (for instance radon in homes) could be considered for intervention.

The BSS therefore provide for more than one way of defining, in national legislation and regulations, the scope of regulatory control of exposures to natural sources, and in practice different countries use different approaches to suit their own situations and preferences.

Exclusion

The decision to exclude is based on whether the exposure is essentially unamenable to control. Apart from some rather obvious examples of excluded exposures given in the BSS (i.e. exposure from ^{40}K in the body, from cosmic radiation at the surface of the earth, and from unmodified concentrations of radionuclides in most raw materials), there is no published international guidance yet on how to interpret the concept of exclusion in regulatory terms. The IAEA may be close to achieving international consensus on activity concentration levels that could be used for applying the concept of exclusion, with the derivation of such levels being based on a consideration of the worldwide distribution of activity concentrations in soil. The activity concentration levels being considered are 10 Bq/g for ^{40}K and 1 Bq/g for all other natural radionuclides. These levels could also be used as clearance levels, i.e. for release of NORM from regulatory control.

Exemption

The principal exemption criteria given in the BSS are that the risks to individuals and the collective impact be sufficiently low as not to warrant regulatory concern or control, and remain sufficiently low in all likely scenarios. Such criteria could provide a (qualitative) basis for exemption of a practice involving work with NORM[8,9]. The BSS also specify criteria based on activity and activity concentration for automatic exemption without further consideration. For natural radionuclides these levels range from 1 Bq/g upwards (mostly 1 or 10 Bq/g) and are intended to apply to the incorporation of natural radionuclides into consumer products or their use as sources or for their elemental properties. Although the numerical values were based on moderate quantities of material, they were derived conservatively and it is suggested

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[8] This is also the view expressed in guidance published by the European Commission (para. 5.3 of Ref. [13]).

[9] The BSS provide numerical dose criteria for exemption without further consideration, but the use of these is not practicable for natural sources — the individual dose criterion of 10 μSv per year is a very small increment to the average natural radiation background and an order of magnitude or two below regional variations.

in Ref. [3] that the activity concentration values could also be used as a means for defining when a practice involving work with NORM, or a source within such a practice, is exempted. Apart from this, there is no published international guidance yet on numerical criteria for exemption of practices or sources giving rise to exposure to natural radiation.

Guidance published by the European Commission [13] establishes a criterion of 300 μSv incremental dose per year for the exemption of work activities involving significant exposure to natural sources. On this basis, the following exemption levels expressed in terms of activity concentrations of radionuclides in the uranium and thorium decay series have been derived[10]: 0.5 Bq/g for ^{238}U, ^{226}Ra, ^{232}Th and ^{228}Th in secular equilibrium with their progeny; 1 Bq/g for ^{228}Ra in secular equilibrium with ^{228}Ac; and 5 Bq/g for ^{210}Pb in secular equilibrium with ^{210}Bi, for ^{210}Po, and for ^{40}K. These activity concentrations are similar to those being proposed within the IAEA as exclusion levels, although the basis for their derivation is quite different.

Exposures automatically included in the system of control

The BSS define the following exposures to natural sources as included within the system of control (unless the exposure is excluded or the practice or source is exempted):

(1) Exposure due to the (deliberate) incorporation of naturally occurring radionuclides into consumer products, or to their use as a radioactive source (e.g. ^{226}Ra, ^{210}Po) or for their elemental properties (e.g. thorium, uranium);

(2) Exposure due to any activity in the nuclear fuel cycle[11];

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[10] These exemption levels have been derived considering both occupational and public exposures, and apply to all materials except wet sludges from the oil and gas industry, for which higher values have been derived.

[11] The mining and milling of radioactive ores fall into this category [3]. Although the term "radioactive ore" is not defined in the BSS (in principle, all ores are radioactive to some extent), it can be taken to mean an ore mined for the purpose of extracting the radioactive elements uranium or thorium.

(3) Public exposure delivered by an effluent discharge or the disposal of radioactive waste arising from a practice involving natural sources;

(4) Occupational exposure to radon, other than exposure incidental to the work that does not exceed the action level for remedial action relating to chronic exposure situations involving radon in workplaces[12].

Exposures specified by the regulatory body as being subject to control

The Safety Guide on Occupational Radiation Protection [3] advises that the regulatory body should first undertake an investigation of the relevant occupational exposure situations to determine the extent of the exposures. For occupational exposures associated with NORM industries (i.e. the mining and processing of raw materials), a suggested approach is then to define levels of activity concentration above which the requirements for practices would apply. It is noted in the guidance that, although these levels define what is included within the system of control, they can effectively act as exclusion or exemption levels defining what is outside of the system of control. The guidance goes on to say that, for practical reasons, the regulatory body may wish to use the levels as the basis for a quantitative definition of radioactive substance and that, as mentioned earlier, the exemption levels of activity concentration given in the BSS for naturally occurring radionuclides could be used for this purpose. The guidance in Ref. [3] also refers to the relevant text in ICRP Publication 75 [14], which concludes with the following recommendations:

- Regulatory bodies should choose activity concentrations of parent radionuclides within the range 1–10 Bq/g to determine whether the exposures

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[12] The action level is established taking into account the benefits and costs associated with the remedial action plan, and is expected generally to be 1000 Bq of ^{222}Rn per cubic metre of air. Examples of workplaces where exposure to radon is incidental to the work include facilities for the mining and processing of ores other than uranium or thorium ores, waterworks, caves, spas, and above-ground workplaces in radon prone areas [3, 8].

from these materials should be regarded as occupational — this range corresponds to worker doses of about 1–2 mSv per year.

- A single generic value or values for specific radionuclides may be chosen, above which an evaluation of the exposures and working conditions should be carried out with a view to determining whether precautions are required to limit exposure of workers.

The Safety Guide [3] also gives guidance on situations involving elevated gamma dose rates due to the presence of NORM in the ground and building materials that make up the workplace, stating that it may be appropriate to apply an approach similar to that for radon exposure — a gamma dose rate of 0.5 μSv/h for a working year would lead to an annual effective dose of about 1 mSv, and this dose rate or some multiple of it might be adopted as an action level for remedial action. As in the case of radon, the approach would be to consider whether the exposure could reasonably be reduced to below the action level (for example, by shielding). Failing this, the numerical value of the action level could be used to define when the requirements for practices apply.

Summary — the emerging international view

The direction is clearly towards the use of activity concentration levels of natural radionuclides in materials as the first step in defining what should be outside of the system of control, whether this be through exclusion or exemption. Consensus seems to be emerging around a figure of 10 Bq/g for ^{40}K and 1 Bq/g for all other natural radionuclides. In countries where activity concentration levels are already in use for this purpose, the numerical values are generally of the same order of magnitude as these figures.

The use of activity concentration levels in materials is, on its own, not enough to decide on what should be subject to control, however, since there is only a very loose correlation between activity concentration and dose. This is illustrated in Figs 1 and 2, which give data for occupational exposure to radon and to dust and gamma radiation, respectively, based on actual occupational exposure measurements made in a selection of NORM industries involving raw materials with moderate activity concentrations. Any trend towards higher doses at higher activity concentrations is very poorly defined. Table I gives some indication of the relative contributions to the total dose.

The data for exposure to radon in Fig. 1 demonstrate that the radon action level (and even the occupational dose limit) can be exceeded during work with materials that are not significantly more radioactive than normal soil. This is, of course, the reason why radon has to be treated separately using as a regulatory criterion the activity concentration of radon in air rather than the activity concentration of its parent radionuclide in the material from which it originates.

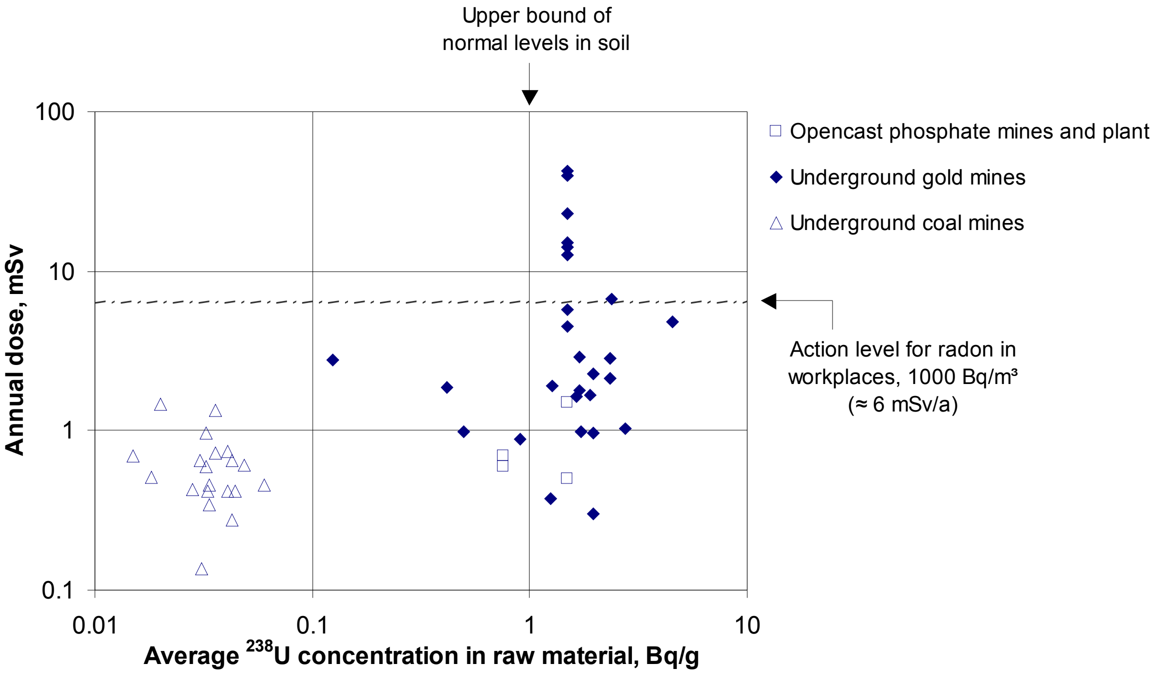

FIG. 1. Some examples of doses received by workers from radon inhalation [15–18]

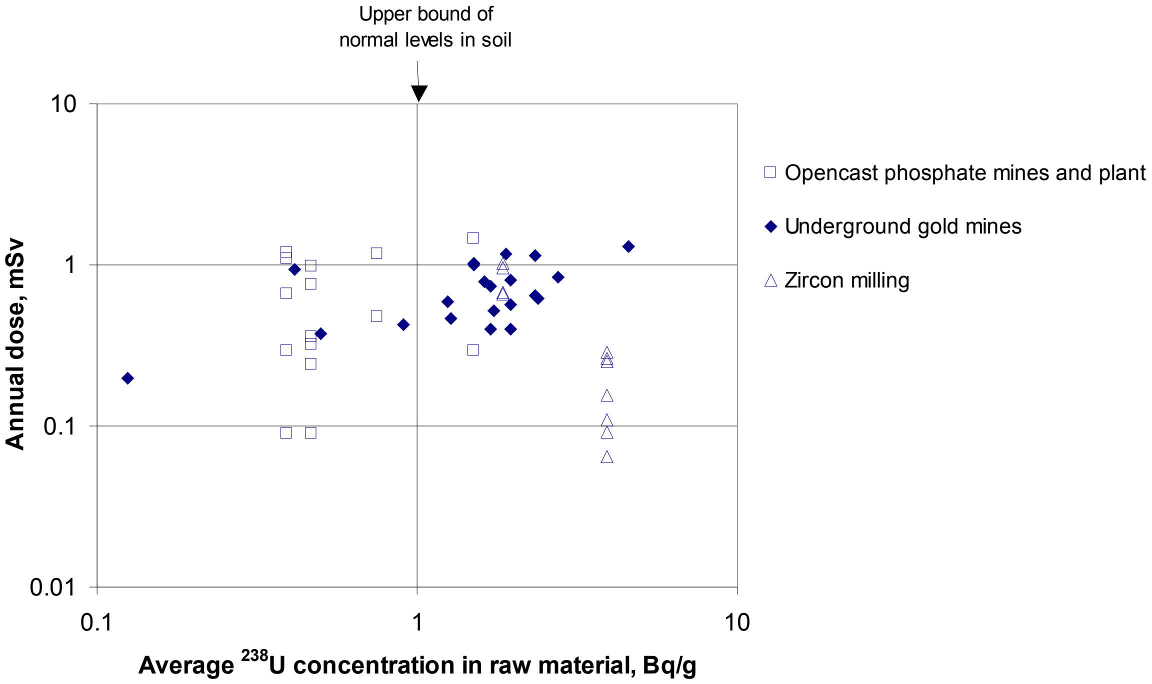

FIG. 2. Some examples of doses received by workers from external gamma radiation and dust inhalation [16, 17, 19–23]

TABLE I. SOME EXAMPLES OF RELATIVE CONTRIBUTIONS TO WORKER DOSES FROM LOW ACTIVITY SOURCES OF NATURAL RADIATION [15–23]

Type of facility	Average total dose, mSv/a (range in parentheses)		Average contribution to dose (range in parentheses)					
			External gamma radiation		Inhalation of dust		Inhalation of radon	
Underground coal mines	1	(0.1–2)	Insignificant		Insignificant		~100%	
Underground gold mines	7	(1–43)	22%	(2–57%)	2%	(0–9%)	76%	(39–98%)
Opencast phosphate mines	1	(0.1–2)	71%	(44–100%)	22%	(0–56%)	7%	(0–32%)
Phosphate bene-ficiation plants	1	(0.1–2)	50%	(12–100%)	37%	(0–88%)	12%	(0–65%)
Zircon mills	0.4	(0.1–2)	57%	(15–85%)	43%	(16–85%)	Insignificant	

The data in Fig. 2 for exposure to external gamma radiation and dust are consistent with the statement in ICRP Publication 75 [14] and the IAEA Safety Guide on Occupational Radiation Protection [3] that work with raw materials with activity concentrations of uranium series radionuclides up to about 1–10 Bq/g is unlikely to result in workers receiving doses exceeding 1–2 mSv per year, even in relatively dusty conditions and close to large quantities of material. Doses received by members of the public are likely to be considerably lower — according to European studies, less than 300 μSv per year [13] (see also Table II below).

Reference to Fig. 2 demonstrates that for exposures to external gamma radiation and dust the use of an exclusion level of, say, 1 Bq/g for uranium series radionuclides will not be effective in screening out all of those NORM activities that do not warrant control — indeed, on the strength of the few data presented, none of the industrial operations in Fig. 2 would appear to warrant control, even though they involve NORM activity concentrations of up to five times the proposed exclusion level. There needs to be a mechanism for examining the non-excluded activities in more detail, particularly those that exceed the exclusion level by only a few times, and determining, using dose as a criterion, those activities that should remain outside the system of control. This mechanism is effectively exemption applied on a case-by-case basis. As to the choice of dose criterion to be used for this purpose, the findings of the Geneva Conference [12], the recommendations of ICRP Publication 75 [14], the guidance in the IAEA Safety Guide on Occupational Radiation Protection [3], and the guidance published by the European Commission [13] all point to a value of the order of 1 mSv per year, perhaps a little higher than this for occupational exposure and a little lower for public exposure.

4. A GRADED APPROACH TO REGULATION

The findings of the Geneva conference highlighted the need for flexibility in cases where some form of regulatory control of exposures was required. In broad terms, the BSS provide for considerable flexibility in the application of its requirements, stating that such application “shall be commensurate with the characteristics of the practice or source and with the magnitude and likelihood of the exposures … Not all the requirements are relevant for every practice or source, nor for all the actions specified …”. In terms of the administrative requirements for practices that do not qualify for exemption, the BSS specify three levels of regulatory control: (i) notification, (ii) notification and registration, and (iii) notification and licensing. Practical application of this concept of a graded approach to regulation will vary from country to country.

Notification

A legal person intending to carry out a practice must submit a notification to the regulatory body of such an intention. This is a requirement in all situations and serves as a basic form of control that can be especially useful for the regulation of many NORM activities giving rise to low doses. It ensures that the regulatory body is at least aware of the practice, even though specific radiation protection measures are not normally needed. The BSS state that "Notification alone is sufficient provided that the normal exposures associated with the practice or action are unlikely to exceed a small fraction, specified by the Regulatory Authority, of the relevant limits, and that the likelihood and expected amount of potential exposure and any other detrimental consequence are negligible".

Authorization by registration

In terms of this requirement, the legal person must, in addition to notifying the regulatory body, apply for an authorization in the form of a registration. This is the less stringent of the two types of regulatory authorization, and is appropriate for many NORM activities where levels of exposure are moderate. The Safety Guide on Occupational Exposure in the Mining and Processing of Raw Materials [10] states that "Registration should provide for the conditions of occupational exposure to be reviewed periodically or in the event of a change in the process that could significantly affect exposures", implying that, as a minimum, exposures must be monitored and recorded.

Authorization by licensing

This is the more stringent of the two types of authorization, and may be appropriate for some NORM activities where levels of exposure are such that the necessary level of protection would not be achieved without the adoption of specific control measures. The BSS require that the mining and milling of radioactive ores (i.e. uranium or thorium ores) be authorized by licensing.

Radiation protection measures

The radiation protection measures needed for a particular operation or process involving NORM will depend on the details of that operation or process and the characteristics of the materials involved. It is not possible to generalize, and the IAEA's approach is therefore to examine the various exposure situations in different industry sectors through the development of the sector-specific Safety Reports referred to earlier. Data are still being gathered, but some examples of information becoming available are given in Table II. Generally, only certain processes within a particular industry sector require protective measures to be taken, and these measures may be fairly simple in nature, such as good ventilation, housekeeping and industrial hygiene, and the use of basic personal protective equipment (PPE). Work involving high activity scales may require respiratory protection to be worn. Chemical processes may require some control over discharges to the environment. These forms of protective measures may already be required under existing industrial health, safety and environmental regulations, in which case the regulatory body responsible for radiation protection may simply need to be satisfied that these measures are adequate for radiological purposes.

TABLE II. SOME EXAMPLES OF EXISTING OR POSSIBLE CONTROL MEASURES FOR INDUSTRIAL PROCESSES INVOLVING NORM

Industry/process	Dose (mSv/a or as stated)		Control measures
	Workers	Public	
Phosphate industry			
Mining/beneficiation [16, 19, 20, 24]	0.1–2	0.02	None (candidate for exemption)

Ore transport and storage [25]	0.1–0.5		None (candidate for exemption)
Thermal phosphorus plant [23, 26] (precipitator dust 1000 Bq/g ^{210}Pb)	0.2–5	0.03	Contamination monitoring/control, PPE, ventilation, decay storage of dust
Phosphorus slag in roads [23, 26]	≤0.6	0.001 –0.06	None (candidate for exemption)
Wet process phosphoric acid plant [24]	0–0.8		Operation: none. Maintenance: possibly control exposure to scale
Oil and gas industry (pipe scale 0.1–15 000 Bq/g ^{226}Ra) [9]			
Gamma exposure during operation	«20		Normally none. Exceptionally distance, time, shielding
Gamma exposure while working on open equipment	0.1–300 Sv/h		Restrict access and occupancy time
Dust inhalation while decontaminating equipment	0.1–1 mSv per gram inhaled		Ventilation, PPE, contamination monitoring/control
Sulphuric acid production from pyrite (scale 100–100 000 Bq/g ^{226}Ra) [27]			
Normal operation	1 (5 max)		None
Maintenance (duration 30 days)	0.4 mSv (max 2.8 mSv)		Minimize exp. time, PPE, reduce scale formation, control disposal of scale
Zircon/zirconia industry			
Zircon milling [21, 22]	0.06–1		Dust control in plant
Zircon in ceramic tiles [21, 28]	0.01–0.5	0.003 –0.06	None (candidate for exemption)
Zircon sand landfill disposal [29]		0–0.1	Restrict disposal to landfill only
Thermal zirconia plant (zircon feed, off-gas filtration system) [21]	0.25–3.1		Dispose of off-gas dust to landfill. Maintenance/demolition: dust control
Chemical zirconia plant (baddeleyite feed) [21]	2.1–3		Minimize exposure to scale, effluent discharge control
Production of Zr chemicals [21]	<0.3–3		Effluent discharge control

5. SUMMARY AND CONCLUSIONS

For exposure to radon and to external gamma radiation from building materials making up the workplace, explicit guidance (based on action levels for remedial action) exists already on what should be inside or outside of the system of regulatory control. For other exposures arising from work involving NORM, consensus seems to be emerging around activity concentrations of 1 Bq/g for uranium and thorium series radionuclides and 10 Bq/g for ^{40}K as criteria for determining whether exposure to NORM should be excluded from regulatory consideration. For materials with activity concentrations above these levels, the regulatory body needs to decide on a case-by-case basis what should be included in the system of control. Published guidance, practical experience and informed opinion suggest that such a decision might be made on the basis of a dose criterion of around 1 mSv/a, perhaps a little more for occupational exposure and a little less for public exposure.

For situations included in the system of control, a graded approach to regulation is needed. The three tiers of regulation provided for in the BSS — notification alone, notification plus registration, and notification plus licensing — all have a role to play in the regulation of work involving NORM. Protective measures need to be matched to the particular process and material involved. Often, such measures need only be fairly simple in nature, and may even be in place already in terms of existing national health, safety and environmental regulations. Appropriate protective measures for specific industrial processes and materials are being identified by the IAEA as part of the development of a suite of Safety Reports and associated training packages focusing on various NORM industry sectors. A Safety Report and training package on the oil and gas sector has already been completed, and Safety Reports on the phosphate, zircon/zirconia and titanium dioxide industry sectors are under development (to be followed, again, by associated training packages). Other NORM industry sectors are to be similarly addressed in future.

REFERENCES

[1] FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS, INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR ORGANISATION, OECD NUCLEAR ENERGY AGENCY, PAN AMERICAN HEALTH ORGANIZATION, WORLD HEALTH ORGANIZATION, International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources, Safety Series No. 115, IAEA, Vienna (1996).

[2] INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, 1990 Recommendations of the International Commission on Radiological Protection, ICRP Publication 60, Ann. ICRP **21** 1–3, Pergamon Press, Oxford and New York (1991).

[3] INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR OFFICE, Occupational Radiation Protection, Safety Standards Series No. RS-G-1.1, IAEA, Vienna (1999).

[4] INTERNATIONAL ATOMIC ENERGY AGENCY, The Application of the Principles for Limiting Releases of Radioactive Effluents in the Case of Mining and Milling of Radioactive Ores, Safety Series No. 90, IAEA, Vienna (1989).

[5] INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR ORGANISATION, WORLD HEALTH ORGANIZATION, Radiation Monitoring in the Mining and Milling of Radioactive Ores, Safety Series No. 95, IAEA, Vienna (1989).

[6] INTERNATIONAL ATOMIC ENERGY AGENCY, Management of Radioactive Waste from the Mining and Milling of Ores, Safety Standards Series No. WS-G-1.2, IAEA, Vienna (2002).

[7] INTERNATIONAL ATOMIC ENERGY AGENCY, Monitoring and Surveillance of Residues from the Mining and Milling of Uranium and Thorium, Safety Reports Series No. 27, IAEA, Vienna (2002).

[8] INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR OFFICE, Radiation Protection against Radon in Workplaces other than Mines, Safety Reports Series No. 33, IAEA, Vienna (2003).

[9] INTERNATIONAL ATOMIC ENERGY AGENCY, Radiation Protection and the Management of Radioactive Waste in the Oil and Gas Industry, Safety Reports Series No. 34, IAEA, Vienna (2003).

[10] INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR OFFICE, Occupational Radiation Protection in the Mining and Processing of Raw Materials, Safety Standards Series No. RS-G-1.6, IAEA, Vienna (2004).

[11] INTERNATIONAL ATOMIC ENERGY AGENCY, Topical Issues in Nuclear Safety (Proc. Int. Conf. Vienna, 2001), Proceedings Series, IAEA, Vienna (2002).

[12] INTERNATIONAL ATOMIC ENERGY AGENCY, Occupational Radiation Protection: Protecting Workers against Exposure to Ionizing Radiation (Proc. Int. Conf. Geneva, 2002), Proceedings Series, IAEA, Vienna (2003).

[13] EUROPEAN COMMISSION, Practical Use of the Concepts of Clearance and Exemption — Part II: Application of the Concepts of Exemption and Clearance to Natural Radiation Sources, Radiation protection 122, Office for Official Publications of the European Communities, Luxembourg (2002).

[14] INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, General Principles for the Radiation Protection of Workers, ICRP Publication 75, Ann. ICRP **27** 1, Pergamon Press, Oxford and New York (1997).

[15] WYMER, D.G., “Radioactivity in South African Coal”, 37th SAAPMB Annual Congress (Conf. Cape Town, 1997), South African Association of Physicists in Medicine and Biology, Pretoria (1997).

[16] OTHMAN, I., AL-HUSHARI, M., RAJA, G., Radiation exposure levels in phosphate mining activities, Radiat. Prot. Dosimet. **45** 1–4 (1992) 197–201.

[17] WYMER, D.G., VAN DER LINDE, A., "An overview of occupational exposures in underground gold mines in South Africa", Radiation Protection and Radioactive Waste Management in the Mining and Minerals Processing Industries (Proc. Conf. Johannesburg, 1995), South African Radiation Protection Society, Mine Ventilation Society of South Africa, South African Institute of Mining and Metallurgy (1995).

[18] WYMER, D.G., "Nuclear regulation of South African mines: an industry perspective", Impact of New Environmental and Safety Regulations on Uranium Exploration, Mining, Milling and Management of its Waste (Proc. Technical Committee Meeting Vienna, 1998), IAEA-TECDOC-1244, IAEA, Vienna (2001) 73–88.

[19] DE BEER, G.P., Radiological Screening Survey of the Foskor Processing Plants, Rep. RAD/R/004, Atomic Energy Commission of South Africa, Pretoria (1994).

[20] DE BEER, G.P., Radiological Screening Survey of the Foskor Processing Plants, Rep. RAD/R/9523, Atomic Energy Commission of South Africa, Pretoria (1995).

[21] SELBY, J.H., Zircon Minerals Committee, personal communication.

[22] HARTLEY, B.M., The measurement of radiation levels in Australian zircon milling plants, Health Phys. **80** 1 (2001) 16–23.

[23] ERKENS, W.H.H., Thermphos International BV, Netherlands, personal communication.

[24] VAN DER WESTHUIZEN, R., Foskor Limited, South Africa, personal communication.

[25] PFISTER, H., PAULY, H., "External radiation exposure due to natural radionuclides in phosphate fertilizers in the Federal Republic of Germany",

Radiological Burden of Man from Natural Radioactivity in the Countries of the EEC (Proc. Seminar, 1979), EU-8-1277, Office for Official Publications of the European Communities, Luxembourg (1979).

[26] ERKENS, W.H.H., “Electro-thermal phosphorus production: Radioactivity in the environment and workplace: Justification, optimisation and ALARA considerations”, Good Radiation Practices in Industry and Research (Proc. 2nd European ALARA Network Workshop, Chilton, UK, 23–25 November 1998, sponsored by CEC DG XII – Research, Nuclear Energy Programme), Office for Official Publications of the European Communities, Luxembourg.

[27] KRUGER, I.D., Occupational exposure in South African metallurgical plants and industries involving naturally occurring radionuclides, presentation to International Atomic Energy Agency Technical Committee Meeting on *The Assessment of Occupational Protection Conditions in Workplaces with High Levels of Exposure to Natural Radiation*, Vienna, 2001.

[28] STRYDOM, R, SELBY, J.H., “Assessment of radiological exposure from ceramic tile glazes containing zircon”, Heavy Minerals 1999 (Proc. Conf. Johannesburg, 1999), South African Institute of Mining and Metallurgy, Johannesburg (1999).

[29] BERNHARDT, D.E., ROGERS, V., Radiological risk assessment for disposal of zircon material in a municipal landfill, Rep. RAE-9507/1-2, prepared for Zirconium Environmental Committee, Rogers and Associates Engineering, Salt Lake City, UT (2000).

A STUDY CONCERNING NORM IN REFRACTORIES INDUSTRIES

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ABSTRACT

A specific study concerning refractories industries has been performed by a group of Italian Regional Environmental Protection Agencies together with the National Agency for Environmental Protection and Technical Services. The aim of this study was to evaluate the environmental impact for some activities dealing with NORM. A radiological survey has been carried out in a Northern Italy company. Activity concentrations measurements by gamma spectrometry (more relevant gamma nuclides of natural chains) and radiochemical analysis (^{210}Pb, ^{210}Po) on raw materials, finished products, residues and treatment water were made.

Information and technical data related to the present working cycle have been collected by means of specific questionnaires, sent to most of the involved factories selected from the sector association's data base.

An estimate of collective effective dose based on a simplified model is made by the combination of the radiological results of the companies survey with information from the questionnaires.

1. INTRODUCTION

A study project about NORM is being developed by the National Topic Centre on Phisical Agents (CTN-AGF), a coordination of Regional Agencies for the Environmental Protection (ARPA), which supports the National Agency for Environmental Protection and Technical Services (APAT) in collecting environment quality information as far as physical pollutants are concerned.

Among the relevant work activities, the refractories industries have been chosen to be studied in detail, because they can use both zircon sands (or zircon silicate flour) and zircon sands based semi-finished products as raw material and it is well known that zircon sands may present elevated natural radionuclides content.

This study has two working plans:

- to evaluate the environmental radiological significance for a specific refractories industry by the determination of ^{40}K and some radionuclides of ^{238}U and ^{232}Th chains and to estimate of the collective effective dose by a simplified model
- to give an overview of the general situation of Italian refractories industries through data from the specific questionnaires, that have been sent to selected refractories factories.

Three laboratories have been involved in this project: ARPAV (Regional Agency for the Environmental Protection of Veneto), APAT (National Agency for Environmental Protection and Technical Services) and University of Urbino.

2. NORM IN A SPECIFIC REFRACTORIES INDUSTRY

2.1 Manufacturing cycle description

The most widespread components of refractories materials are Alumina, Zirconia and Silica.

The typical manufacturing cycle can be described in this scheme:

- raw materials preparation (casting into moulds of sand, graphite or metal)
- fusion in an electric furnace
- grinding and finishing

Raw materials may be zircon sands/silicates or semi-finished zircon silicates based components (for instance “mullite-zircon” or scraps).

The products are obtained by the solidification of a mixture which has been melted in an electric furnace and casted in liquid state into moulds.

During this step the uranium chain may be broken, with consequently ^{210}Pb and ^{210}Po enrichment in residual dust, due to volatilization at high temperatures of fusion.

After fusion products are finished through sand-blasting and scraps are grinded to enter the manufacturing cycle again; residual dusts are generated in this stage.

Waste water and sludge coming from different sectors of the factory are formed as residues too.

Only dusts produced by sand-blasting and waste water (after depuration) are discharged, instead of fusion dusts and sludges are recycled into manufacturing process.

2.2 Samples and radioanalytical and radiometric measurement methods

In year 2003 some activity concentration measurements have been carried out in raw materials, products and residues of a selected refractory materials industry.

Three laboratories have made the analysis: ARPAV, APAT and University of Urbino.

The determined radionuclides are ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{235}U, ^{232}Th, ^{40}K.

ARPAV measurements have been performed by gamma spectrometry with high resolution germanium detectors.

^{238}U has been assessed through its decay product ^{234m}Pa; ^{226}Ra through its decay products ^{214}Pb and ^{214}Bi and, in this case, secular equilibrium has been restored by keeping samples in a sealed aluminium beaker for a month. Also ^{232}Th (through its gamma-emitting decay products), ^{235}U and ^{40}K determinations have been made.

The coincidence summing, in particular for ^{214}Bi, and self-attenuation effects, have been corrected through GESPECOR software.

The determination of ^{238}U, ^{210}Pb and ^{210}Po activity concentration have been carried out by University of Urbino and APAT. The radioanalytical methods were based on: a) the sample pretreatment, b) the radionuclide separation, c) the source preparation . Finally ^{238}U and ^{210}Po were counted by α-spectrometry, ^{210}Pb by a low background beta counter.

2.3 Results and discussion

Table 1 shows the activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{235}U, ^{232}Th, ^{40}K in refractory raw materials, products and residues.

Percentage deviations in analysis of same samples, that on average are 14 for ^{238}U, 14 for ^{210}Pb and 10 for ^{210}Po, may represent an estimate of assessment uncertainty; in effect they seem to be comparable with single measurements uncertainties.

^{238}U series content, for zircon sand, fairly agrees with literature values; elevated ^{210}Pb and ^{210}Po contents in fusion furnace dust are found (because of enrichment due to volatilization for high temperatures of fusion) and other natural radionuclides contents are modeste (this is also attested by relevant ^{210}Po content in outgoing gas of fusion furnace filter).

On the contrary, dust generated by refuse grinding shows high activity concentrations of all natural radionuclides.

The majority of the finished products presents significative values of ^{238}U series concentrations, with ^{210}Pb and ^{210}Po depauperation, bacause of their volatilization at high temperatures during fusion process.

Moderate activity concentrations of all natural radionuclides are shown in product 4, due to the absence of zircon silicate in this sample, that is composed of an Alumina and Silica mixture.

The activity values in sludges, coming from the complete water depuration process, are elevated whereas in waste water, after the depuration process, are negligible.

In general radionuclide concentrations of ^{232}Th chain show higher values than environmental levels, but lower values than ^{238}U chain.

Table 8 – Activities concentrations (Bq/kg) in raw materials, products and residues.

SAMPLE	^{238}U***	^{226}Ra*	^{210}Pb**	^{210}Po**	^{235}U*	^{232}Th*	^{40}K*
Zircon sand	3613 (10,2)	3219 (6)	2707 (7,4)	2748,0 (23,3)	137 (7)	517 (6)	0 (36)
Dropping system dust generated by fusion furnace	358,5 (17,6)	147 (6)	21050 (18,8)	35000 (5,7)	20 (10)	27 (6)	10 (17)
Fusion furnace filter	-	-	n.d.	28000 (25)	-	-	-
Dropping system dust generated by refuse grinding	1191 (21,7)	1046 (6)	1033,5 (4,0)	1293,5 (12,3)	59 (9)	178 (6)	255 (6)
Refuse grinding filter	-	-	n.d.	6100 (25)	-	-	-
Product 1	1701,5 (2,9)	1400 (6)	951,5 (7,3)	1088,5 (7,7)	82 (9)	310 (6)	9 (18)
Product 2	1751 (13,9)	1638 (6)	752,5 (8,7)	684,5 (2,4)	91 (8)	262 (6)	0 (38)
Product 3	1714,5 (7,2)	1481 (6)	1343,5 (10,8)	1352,5 (24,9)	82 (9)	250 (6)	23 (13)
Product 4	19,5 (35,9)	8 (6)	31,3 (43,8)	46,0 (2,0)	1 (31)	2 (7)	81 (6)
Sludges	1635 (3,3)	1496 (6)	1166,5 (14,3)	1176,5 (2,7)	88 (7)	238 (6)	27 (11)
Waste water	-	< 0,38	n.d.	0,0044 (25)	< 0,5	< 0,15	< 1,89

* Gamma spectrometry analysis by ARPAV (percentage uncertainty at 68% confident level in brakets).

** Values represent the average of University of Urbino and APAT radiochemical analysis (percentage deviation of two values from the average in brakets).

*** Values represent the average of ARPAV gamma spectrometry analysis and APAT radiochemical analysis (percentage deviation of two values from the average in brakets).

2.4 Estimate of collective effective dose by a simplified model

An estimate of the collective effective dose to the population living near the plant due to the emissions of dusts from fusion and grinding stacks has been made based on the simplified model given in UNSCEAR Report of 1982 ([1]: par. 1B Annex C, pages 111-113).

The model considers two stages of exposure: 1) direct inhalation during the passage of the cloud; 2) introduction (ingestion of contaminated food and inhalation of resuspended material) and external irradiation, after deposition.

In the first case, the inhalation dose for the population living in the plant area is calculated based on the time integrated activity concentrations in that area from the whole nuclides release. The activity release from two stacks has been computed multiplying dust activity concentrations (Table 2) by the dust emitted per year through the stacks (191 and 198 kg/y, respectively). For ^{222}Rn the dose added by plant release is calculated by comparison to the inhalation dose due to natural emanation from soil: all radon contained in processed zircon sands (2320 t/y) is assumed to be released in air. Some parameters have been updated with respect to UNSCEAR Report of 1982: age weighted inhalation effective dose coefficients and breathing rates come from UNSCEAR Report 2000 (table 17 page 127 and par.153 page 107 of Annex B).

In the second case, the model perfoms dose calculation due to deposited activity by comparison with doses resulting from the natural presence of radionuclides in soil. Apart from some fixed parameters [1], significant used data are: natural soil concentrations [2] of 35 Bq/kg for ^{238}U chain, of 30 Bq/kg for ^{232}Th chain and of 400

Bq/kg for ^{40}K, age weighted natural committed effective doses for inhalation and ingestion of various radionuclides ([2]: tables 17, 18 Annex B), age weighted external irradiation dose rates due to natural content of ^{238}U and ^{232}Th series and of ^{40}K in soil ([2]: table 6 Annex B), natural individual committed effective dose for inhalation of ^{222}Rn of 470 microSv/y [2].

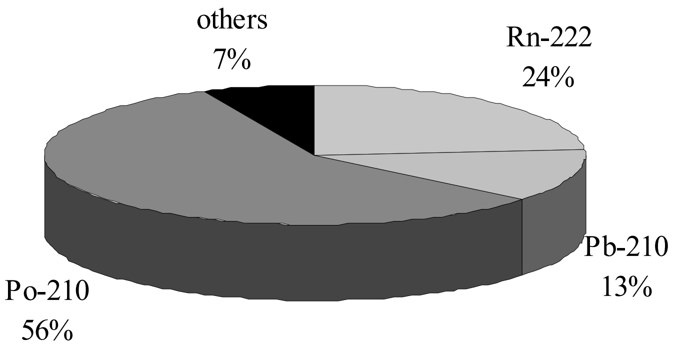
Table 9 - Collective committed effective dose (manSv/y) due to a refractory materials plant.

radionuclides	passage of the cloud	deposition			total
		ingestion	inhalation	external irradiation	
^{238}U	3,57E-06	7,39E-08	6,21E-09	3,03E-05	1,12E-05
^{234}U	4,29E-06	8,28E-08	7,69E-09		1,19E-05
^{230}Th	1,61E-05	1,72E-07	1,42E-08		2,39E-05
^{226}Ra	3,34E-06	1,83E-06	5,94E-09		1,27E-05
^{222}Rn	1,70E-04		1,07E-04		2,78E-04
^{210}Pb	1,87E-05	1,15E-04	1,64E-05		1,50E-04
^{210}Po	9,30E-05	5,73E-04	8,09E-06		6,74E-04
^{232}Th	3,70E-06	1,65E-08	3,85E-09	5,27E-06	5,48E-06
^{228}Ra	4,66E-07	9,62E-07	9,62E-10		3,18E-06
^{228}Th	6,53E-06	1,14E-08	1,33E-08		8,31E-06
^{220}Rn			1,60E-06		1,60E-06
^{235}U	1,95E-07	3,60E-09	3,27E-10		1,98E-07
^{40}K				4,84E-07	4,84E-07
Total	3,20E-04	6,91E-04	1,34E-04	3,60E-05	1,18E-03

Table 2 and figure 1 resume the results of model estimates. The total committed collective effective dose due to the plant emissions is about 1.2 man·mSv/y. From the ratio of the collective dose to the population living in the plant Municipality, a committed effective dose per caput of about 0.3 microSv/y results, far below the action level of 300 microSv indicated by the Italian law [3].

The most significant exposure pathway is the ingestion of contaminated food after deposition; the nuclides that contribute most are (in descending order): ^{210}Po, ^{222}Rn and ^{210}Pb.

More accurate models, however, are to be run (taking into account actual site situation near the plant, ..) given the simplified nature of the model here used.



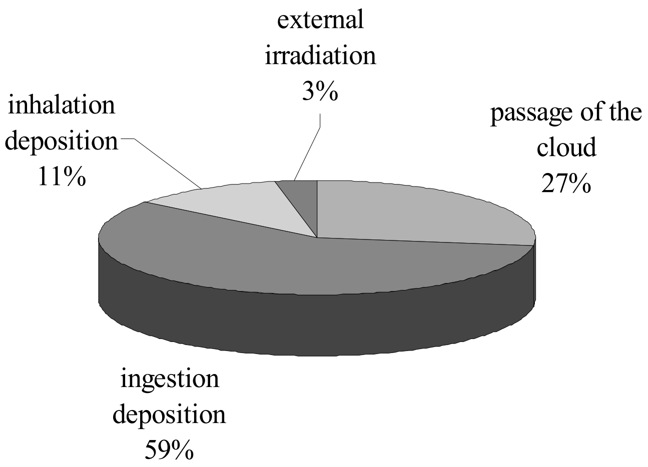


Figure 1 – Exposure radionuclides and pathway contributions.

3. NATIONAL OVERLOOK CONCERNING NORM IN REFRACTORIES INDUSTRIES

The Italian refractories industry is made up of 39 companies, 20 of which join the main sector association, Assopiastrelle (75% market representativity).

In 2002 the refractories manufacturing production amounted to 556.400 ton; the main sector using refractories is the steel industry followed by lime and cement, ceramics, non ferrous metals, glass, energy and petrochemicals.

Ten companies belonging to Assopiastrelle use zircon sands or semi-finished components zircon silicates based in processing, but only two of them are concerned in significative amounts of zircon sands utilization (thousand of tons) [4].

This information and other technical data, related to the present working cycle, have been collected by means of specific questionnaires, sent to the involved factories selected from the sector association's data base.

The questionnaire is divided into four forms, regarding respectively:

- private data of company and all its plants
- type, place of origin, quantity and storage of raw materials involved with zircon sand and silicate.
- type, quantity and caratheristics of output involved with zircon sand, silicate and osside
- quantity of working process residues (dust, sludge and waste water) and technical data of the emissions (for instance: temperature, height and flow of stacks)

On the basis of this preliminary survey, the consumption of zircon sand/silicate or semi-finished components zircon silicates based as raw materials amounted to about 45.000 tons in year 2003.

REFERENCES

1. UNSCEAR, 1982, Sources and Effects of Ionising Radiation, United Nations, New York.
2. UNSCEAR, 2000, Sources and Effects of Ionizing Radiation, United Nations, New York
3. D.Lgs. n° 241/00 "Attuazione della direttiva 96/29/EURATOM in materia di protezione sanitaria della popolazione e dei lavoratori contro i rischi derivanti dalle radiazioni ionizzanti", Suppl. ord. G.U. n. 203 del 31/08/00.
4. Assopiastrelle, CerAnnuario, 2003-2004.

GRAIN SIZE IN RADIOMETRIC MEASUREMENTS OF GROUND

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Grain size in the known procedures of radiometric measurements of ground ranges from 0.043 mm to 0.25 mm. In order to discuss the proper grain size of the ground sample to be measured one must first apply to the definition of ground in radioecology.

There are many classifications of grounds, which differ for the various branches of science and industry (geology, agriculture, industrial construction, etc.). Two main questions to be answered are:

- either ground is composed only by clay and sand or it includes silt (dust), too:
- what are the border grain sizes of ground components.

The reasons for distinguishing a group of sands are mineral composition (mean contents of silica and feldspars in sand are 70 % and 15 %, respectively), looseness (friability), water-permeability and grain size. Upper border of the grain size of sand is 2 mm. Thinner fractions are usually monocrystals or their fragments, whereas larger fractions are in fact accretions of various mineral species, i. e. fragments of rocks. Lower border of grain size is 0.05 - 0.0625 mm. These are the thinnest fractions, which can be obtained by dry sieving. Particles of this size in dry state are still keeping looseness. Thinner fractions can be obtained only by using sedimentary methods. They are gradually being enriched by clay minerals and as a result they gain properties of clay such as sorption ability and a property of ionic exchange. Mean contents of clay minerals and silica in clays are 64 % and 34 %, respectively.

There are no evident reasons for distinguishing a group of silts. They are intermediate in composition between clays and sands containing mainly silica, feldspars, clay minerals, carbonates and micas. They are intermediate in grain size, too. But their physical properties are much closer to those of clays. Being humid, they show fluidity as well as coherence. Silts have a property of ionic exchange, some plasticity, sticky state, linear shrinkage, temporary resistance to pressure. These properties are of course weaker than those of clays but they are not peculiar to sands at all.

Thus for radioecologist who deals with radiometric measurements ground is a poly-dispersive system composed by sand and clay. It is free of organic matter unlike soil. Grain size of sand is 0.0625-2 mm. Thinner fractions are called clay.

Numerous radiometric measurements of clay and sand obtained by sieving of natural grounds sampled randomly in Moscow region were fulfilled. They show significant distinction between clay and sand activities (Table 1). Supposedly the activities of silt would have been intermediate if they had been measured.

Table 1. Integral specific activities of clay and sand in Moscow region

	alpha, Bq/kg		beta, Bq/kg	
	mean activities	square deviation	mean activities	square deviation
sand	103	54	110	31
clay	894	164	1081	96

(Radiometer – HT-1000 Canberra. Weight of measured sample is 1 g. Time of measuring is 1500 sec).

The second factor that should be taken into account concerning grain size of the sample to be measured is peculiarities of radiometric measurements. They are known to be relative, i. e. the activity of the measured sample is calculated using the known activity of the standard sample or the sample of comparison. It means that certain demand to the sample being measured is correspondence of its properties including grain size to the properties of the standard sample.

But it is possible to create the standard sample with any physical properties and radionuclide composition. Moreover, it is evident that the contribution of grain size non-correspondence to combined uncertainty of measurement can be neglected in comparison to radionuclide composition non-correspondence.

The most important factor leading to the right choice of grain size in radiometric measurements is existence of three types of radioactivity.

Natural radioactivity is distributed homogeneously through the bulk of sample. It is either nuclides in crystal structure of minerals (K in $KAlSi_3O_8$) or isomorphous replacement in crystal structure (Ra in $BaSO_4$, Th in $ZrSiO_4$, U in $CePO_4$). Model radiometric measurements of the same sample with grain size ranging from 0.125 mm to 2 mm do not show significant distinction between specific α- and β-activities in spite of increasing of specific surface (Table 2). That is why there is no reason to grind monocrystal grains.

Table 2. Integral specific activities of various fractions of the four samples of ground

Fractions, mm	Integral specific activity, Bq/kg							
	sample 1*		sample 2		sample 3		sample 4	
	Σα	Σβ	Σα	Σβ	Σα	Σβ	Σα	Σβ
< 0.125	< 4	< 69	344	893	749	824	811	739
0.125-0.16	< 4	< 69	272	< 69	148	402	312	313
0.16-0.25	< 4	< 69	< 4	913	437	392	312	590
0.25-0.37	< 4	< 69	< 4	913	125	392	< 4	590
0.37-0.5	< 4	< 69	62	541	499	432	437	442
0.5-0.7			< 4	435	704	559	< 4	267
0.7-0.8			187	327	125	516	312	318
0.8-1			62	144	62	332	< 4	228
1-2			< 4	129	375	268	125	74

* - pure silica sand.

(Radiometer – HT-1000 Canberra. Weight of measured sample is 1 g. Time of measuring is 1500 sec).

Artificial radioactivity is caused by atmospheric fallout presenting nuclides in dynamic form, or by “hot” particles which are commonly uranium and plutonium oxides (silicates) and also ^{14}C. If we grind “hot” particle its fine subparticles will cover non-active grains of matrix that will lead to increasing of surface contamination and as a result – to increasing of specific radioactivity.

Secondary radioactivity is a result of changes of nuclides concentration in grounds owing to weathering, infiltration, precipitation and other natural processes. Both natural and artificial nuclides can be involved in these processes. Nuclides occur here preferentially in sorbed form on the grain surface as salts, hydroxides and complex compounds. This is another kind of inhomogenity, not so sharp one. Grinding such grains increases specific surface, decreasing specific radioactivity.

Preparing a sample of ground to measurements one must take into account its poly-dispersivity and to provide its granulometric representation to the respect to the whole bulk of the initial sample. It looks like this. The initial dried sample undergoes careful grinding in order to decompose it onto the individual crystals and sieving resulted in obtaining a fraction of sand and a fraction of clay. Both fractions are weighed and their correlation in initial sample is calculated. “Proportional” sample must be prepared for measurements by successive reduction of the both fractions. “Proportional” sample has the same correlation of fractions as the initial sample does. The importance of “proportionality” of the sample to be measured is conditioned by the following. Tight mutual relation of the mineral composition of the rock to the size of its grains is fixed. Chemical composition of the rock depends not only on its mineral composition but on granulomertic composition, too. Physical properties of rock, e. g. density and sorption ability as well as crystal-chemical properties, e. g. isomorphous capacity depend obviously on the chemical and mineral composition of the rock. It means that providing granulometric representation one can believe with high probability that representativity of the other parameters is provided, too.

The importance of “proportionality” is conditioned statistically, too. The character of distribution (normal, logarythmic, or more complicated) of activity upon the fractions in the initial natural sample is principally unknown but it is kept in the sample to be measured if we prepare it the way described above. The more we grind or rather mill the initial sample destroying individual crystals, the closer to the normal distribution of activity approaches. The result of such a procedure is a sum of thin particles of absolutely equal size with absolutely normal distribution of activity. It is obvious that such a situation is impossible if one deals with the sample of ground containing “hot” particles.

Thus the whole bulk of the initial sample should be driven to mono-crystal state, i. e. grain size does not have to be fixed. It allows to keep granulometric representativity of the sample to be measured – the easiest kind of representativity which can be provided in laboratory.

TEST THRESHOLDS FOR ASSESSMENT OF POSSIBLE GROUNDWATER CONTAMINATION AT SITES CONTAMINATED WITH RADIOACTIVE MATERIALS

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Abstract

At several sites in Land Brandenburg the ground is contaminated with natural radionuclides, especially thorium from former industrial processes. Such type of contamination is regulated neither in the Federal Ordinance on Soil Protection and Contaminated Sites (BBodSchV) nor in the German Radiation Protection Ordinance (StrlSchV). However, the European Basic Safety Standards Directive specifies that areas of former practice or work that are a source of permanent risk to people have to be demarcated and controlled. If necessary, intervention measures need to be carried out and access must be restricted. Therefore treatment of such cases requires technical regulations and supporting instructions to facilitate correct decisions by the relevant authorities. Such regulations must be conform with the existing regulations, especially the BBodSchV and guidelines of urban land use planning.

When assessing existing situations, the exposure path “groundwater” is of particular significance for any decision-making. Suitable criteria and instructions were derived in order to identify for this special path those areas that can be considered uncontaminated and therefore exempt from further radiological investigations and from any restrictions concerning land use planning. The methodical approach corresponds to the leachate forecast according to BBodSchV. The results obtained are presented in the paper.

Introduction

Several sites in Brandenburg are contaminated with residues from former thorium and uranium production or use. Such type of contamination is regulated neither in the Federal Ordinance on Soil Protection and Contaminated Sites (BBodSchV) nor in the

German Radiation Protection Ordinance (StrlSchV). Nevertheless, the risks resulting from such contaminations must be assessed for any decisions concerning planning and use of the land. Therefore, the Environmental Protection Agency of Brandenburg initiated a study /1/ with the following aims:

- Derive test thresholds for assessment of sites with radioactive contaminants for potential groundwater contamination by radionuclides,
- Develop a guideline for application of these test thresholds in a stepwise investigation of suspicious sites.

It was required that the test thresholds should differentiate between soils that can be classified as uncontaminated and those that must be investigated in greater detail, and that the test thresholds should be based on measurable values related to soil, leachate or groundwater.

Radionuclides – Harmful substances of a special kind?

Thorium and uranium are natural radioactive elements. If their concentrations cause a significant increase in exposure, they cannot be disregarded from the radiation protection point of view (EU Directive 96/29 Title VII).

Due to their special status in environmental legislation and a sensitive awareness of the public, radionuclides are often seen as a special kind of harmful substances different from “common” contaminants. However, the comparison between natural radionuclides, organic contaminants (e.g., PAH) and heavy metals given in Table 1 reveals some general similarities of these contaminant groups. All of them are mixtures of components with different constituents. In soils contaminated with thorium or uranium these radionuclides are isotopes of U, Th, Ra, Pb, Po.

Table 1: Comparison of some basic attributes of radionuclides, organic contaminants (here: PAH), and heavy metals

	Natural radionuclides	**PAH**	**Heavy metals**
Number of substances	36 radionuclides	16 compounds (EPA)	ca. 20 elements
Relevant number of substances in water	5 – 7 (^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po; ^{228}Ra, ^{228}Th)	6 – 8	6 – 8
Temporal changes of total amounts	Physically exact calculation, not influenced by any other factors	Depending on many factors	No change
Toxicology Toxicological evaluation	Cancerogenic Described by dose coefficients	Cancerogenic Described by different toxicological factors	Various Described by different toxicological factors

Chemically, most of the natural radionuclides are heavy metals and their migration in soil and groundwater proceeds in a way similar to heavy metals. As the radionuclides belong to different chemical elements, their concentration in water reflects the different mobility of these elements under the specific geochemical conditions.

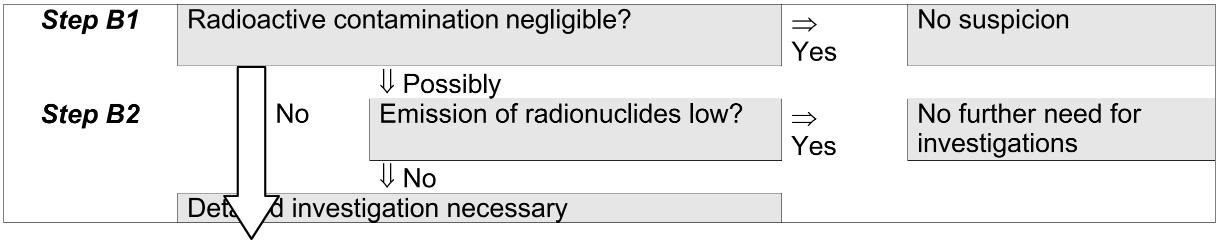
Therefore, radionuclides generally can be considered similar to other contaminants, and the concepts of soil protection can be applied to them, too.

However, a few peculiarities have to be considered: Firstly, the nuclides are members of the uranium or thorium decay series; this means that the decay and increase of radionuclides proceed in a physically exact way (parameter half-life $T_{1/2}$ or decay constant $\lambda = \ln(2)/T_{1/2}$) and are not influenced by any physical, chemical or biological factors. Secondly, radiological risk assessment can be made according to a well established system of consumption rates, dose coefficients and dose limits (“dose concept”). This makes it somewhat easier to assess certain situations than in the case of many common contaminants.

Derivation of test thresholds – Methodological aspects

As to the principles of soil protection, the “risk threshold in the worst case” was used as a general criterion to derive threshold values. A two-step approach was used for transfer of this principle to an applicable concept. The general scheme of the approach is shown in Fig. 1.

Fig. 1: General scheme for assessment of radioactive soil contaminations with regard to groundwater



In step “B1” the soil is assessed for significant radioactivity that may affect the groundwater. If the specific activity is sufficiently low, any suspicion can be excluded and the soil is declared uncontaminated. On the other hand, if the activity is enhanced above test threshold values, the contamination will be classified as significant with a need for detailed investigation.

This, however, oversimplifies the matter of differentiating only between “no suspicion” and “significant contamination”. Therefore, step “B2” is included in the scheme to be used for cases that are characterized by slightly enhanced soil activities. According to the aims of this approach, the possible transfer of radionuclides by seepage water into the groundwater is checked in the step “B2”.

The test thresholds are derived as specific activity (Bq/g) in soil or activity concentration (Bq/l) in seepage water which yield a defined ingestion dose when drinking groundwater. The values were derived according to the rules of leachate forecast, using the following steps:

- Estimation of radionuclide concentration within the contaminated soil layer in the vadose zone (“Source Term”),
- Calculation of radionuclide concentrations at the soil – groundwater interface by a transport prognosis,
- Risk assessment by calculating ingestion doses for persons as a measure of exposure,
- Derivation of test thresholds by relating the doses to the limits.

This approach was applied to an area with:

- Sandy soils and an unconfined aquifer,
- Water table about 2 – 4 m below surface,
- Various types of radioactive soil contamination, mainly thorium ores (monazite), residues from previous thorium extraction from the ores and partly thorium compounds; residues from processing uranium ores occur in some places, too /2/.

Different distributions of contamination in soil were reduced to two case scenarios:

- Contamination close to or in contact with groundwater; the thickness of the uncontaminated horizon is negligible (x = 0),
- Contamination significantly higher than groundwater; assumed thickness of uncontaminated horizon: x = 2 m.

Other contaminants from previous industrial production were factored out, i.e., that means any possible cross-effects were not considered in the risk assessment. Due to the very low level of radiological doses used in this study, such approach is passable. It should be pointed out that the described approach is focussed on the assessment of potential groundwater contaminations originating from soil. Therefore, the values derived are not applicable to the assessment of risks from ground-borne gamma radiation, inhalation of dust or ingestion of soil particles. If necessary, these exposure paths must be assessed separately. They also cannot be used without the specific scenarios given above.

Determination of source term

The first process to be described is the transfer of radionuclides from the solid to the liquid phase, i.e., from soil material into water. This source term was determined from measurements of the radionuclide concentration “C” (Bq/m³) in distilled-water extraction (DIN 38 414-4, S4) of soil samples of specific activity “a” (Bq/g). A transfer factor:

$$TF(i) = C_i / (a_i \cdot 1000) \qquad (1)$$

for the relevant radionuclides was estimated from the measuring results obtained. The values derived by summarizing the results are shown in Table 2.

The transfer factor can be used to calculate the nuclide concentration of seepage water within a contaminated soil layer according to:

$$C_i = TF(i) \cdot a_i \cdot 1000 \qquad (2)$$

It is important to note that the transfer factor does not correspond with the inverse of the distribution coefficient k_d used in the transport model (see below). The transfer factor is a phenomenological figure characterizing the transfer of radionuclides from bulk soil into seepage water, while the k_d-value characterizes the sorption at the surface of minerals.

As in radionuclide analysis at least 1 – 2 litres of water are required to obtain sufficiently low detection limits, the leachate experiments could not be carried out with the “BSE”-method (DIN V 19735).

Table 2: Parameters of radionuclide mobilization and transport used in the model calculations

Nuclide	$T_{1/2}$	TF	k_d	R	$\Lambda_{migr.}$	Kind of migration
	[a]	[g/m³]	[m³/g]	´--	[m]	
^{232}Th	1.4 E+10	100	1.0E-03	4.5E+03	>> 1000	Isolated
^{228}Ra	5.8	250	1.0E-05	45	0.19	Isolated
^{228}Th	1.9	100	1.0E-03	4.5E+03	<0.01	Coupled
^{238}U, ^{234}U	4.4 E+9 2.5 E+5	500	1.0E-05	45	>> 1000	Isolated
^{226}Ra	1600	250	1.0E-05	45	52	Isolated
^{210}Pb	22.3	200	1.0E-04	4.5E+02	0.07	Coupled
^{210}Po	0,38	100	1.0E-04	439	0.001	Coupled

Transport prognosis

The second process to be described is the transport of radionuclides dissolved in seepage water. The fundamental value of this process is the seepage velocity v_a. In the area studied, v_a was estimated as about 1.6 m/a.

Two mechanism influence the travel velocity of a real migration front: dispersion increases the velocity, but retardation decreases it. Under steady-state conditions only retardation takes effect. Assuming a linear equilibrium approach with a distribution coefficient k_d, the retardation factor R is:

$$R = 1 + \rho \frac{n-1}{n} k_d \qquad (3)$$

with ρ - grain density, n – porosity.

The k_d-values used for calculating R (see Table 2) were adopted from the literature /3/.

Two different models must be used to determine the transport of decay-series radionuclides in seepage or groundwater.

In **Model 1 ("isolated migration")** a type of radionuclide "i" is assumed to migrate in an "isolated" manner, i.e., transport proceeds without any significant radiogenic production from a precursor. The concentration $C_{i,0}$ of such radionuclide in water decreases due to radioactive decay exponentially with the distance x according to:

$$C_i = C_{i,0} \cdot \exp\left(- \frac{x}{\Lambda(i)_{migr}} \right) \quad (4)$$

The parameter Λ_{migr}

$$\Lambda_{migr} = \frac{v_a}{R_i \cdot \lambda_i} \qquad (5)$$

characterizes the length of migration, i.e., the distance that reduces the concentration by the factor 1/e due to radioactive decay (λ - decay constant = $\ln(2)/T_{1/2}$, see Table 2) and retardation R.

This model is applicable to long-lived radionuclides without dissolved precursors. Typical examples of such nuclides are ^{238}U, ^{234}U, ^{232}Th and ^{226}Ra.

The parameters compiled in Table 2 show very low migration lengths (^{210}Pb, ^{210}Po, ^{228}Th). These nuclides will not arrive at the groundwater table if the distance between contaminated horizon and groundwater is more than 1 m.

However, due to radiogenic production the short-lived daughter nuclides are generated so fast that an activity equilibrium exists in the entire water–rock system. Consequently, the short-lived nuclides must be taken into account when a long-lived precursor reaches the groundwater table. In such case the concentration of dissolved radionuclides results from the different sorption–desorption behaviour of the type of radionuclide involved. This effect is described by **Model 2 ("coupled migration")** /4/.

The concentration of daughter nuclide "j", which migrates coupled on the precursor "i", can be calculated from:

$$C_j = \frac{R_i}{R_j} \cdot C_i \quad (6)$$

For application of both models a distinction must be made between radionuclides which migrate in an isolated manner and those which are regarded “coupled”. In the case under review two migration groups were considered:

Migration group 1: ^{226}Ra as long-lived precursor with isolated migration; ^{210}Pb, ^{210}Po as coupled daughter nuclides.

Migration group 2: ^{228}Ra as long-lived precursor with isolated migration; ^{228}Th, ^{224}Ra as coupled daughter nuclides. ^{228}Ra was stated as a precursor because its precursor ^{232}Th usually is not dissolved and the radiological relevance of ^{228}Ra is very high.

The long-lived nuclides ^{238}U, ^{234}U, ^{232}Th were involved, too.

The concentration C_i of an “isolated” radionuclide “i“ in the zone of transition into the groundwater (“site of assessment”) resulting from the soil contamination a_i is calculated according to:

$$C_i = TF(i) \cdot a_i \cdot \exp\left(- \frac{x}{\Lambda(i)_{migr}} \right) \quad (7)$$

The corresponding concentrations of the “coupled” radionuclides are obtained from equation (6).

Calculation of doses

As mentioned in Table 1, radionuclides are classified as cancerogenic substances. The radiation effects are quantified with a linear non-threshold dose-effect relationship. The risk resulting from ingestion of radionuclides with concentration C (Bq/l) can be evaluated by calculation an ingestion dose H_{ing} (SI unit Sievert, Sv):

$$H_{ing} = VR \cdot \sum_i DK_i \cdot C_i \quad (8)$$

with VR – consumption rate (l/a), DK – dose coefficient (Sv/Bq). Consumption rates and dose coefficients depend on the age of the persons concerned. They are defined in the German Radiation Protection Ordinance (StrlSchV).

For a simple comparison, dose factors ($VR \cdot DK_i$) for drinking water consumption of the most sensitive age group (0 –1 years) are given in Table 3. It is obvious that ^{228}Ra, ^{210}Pb and ^{210}Po are very highly relevant to possible doses.

Table 3: Dose factors for drinking water (children, age 0 – 1 years)

Nuclide	**$VR \cdot DF_i$** (mSv/a) / (Bq/l)	**Nuclide**	**$VR \cdot DF_i$** (mSv/a) / (Bq/l)
^{238}U	0.058	^{232}Th	0.78
^{234}U	0.063	^{228}Ra	5.10
^{226}Ra	0.80	^{228}Th	0.63
^{210}Pb	1.43		
^{210}Po	4.42		

Reference limits

Using the models described above, a relationship can be established between a specific soil activity and the potential dose resulting from drinking the water. For derivation of the threshold values it is necessary to relate these doses with reference limits.

In Germany there exists one general concept for deriving threshold values in seepage water. It was developed by the “Länderarbeitsgemeinschaft Wasser” (LAWA) and defines soil contaminations as harmless in relation to groundwater if the contaminant concentration in the seepage water is below the limits of the German

Drinking Water Directive (TrinkwV) and ecological effects can be excluded. If this concept is used, the primary reference dose is 0.1 mSv/a.

The German Radiation Protection Ordinance defines 1 mSv/a as the general protection level for members of the public. This level refers to all types of exposure caused by special situations with enhanced concentrations of natural radionuclides. As drinking of water covers only one exposure path, the German Radiation Protection Commission (SSK) used 0.5 mSv/a as reference value already in a former recommendation /6/.

Both dose values (0.1 mSv/a and 0.5 mSv/a) were used to assess soil contamination. This resulted in a two-level concept of threshold values. Specific activities or radionuclide concentrations corresponding to the level of 0.1 mSv/a are termed Lower Assessment Values (Untere Beurteilungswerte, “UBW”), those of level 0.5 mSv/a are termed Upper Assessment Values (Obere Beurteilungswerte, “OBW”).

Results

Starting out from the general concept (Fig. 1), the data (see Table 2), models and reference limits, threshold values were derived for every single radionuclide. For practical use these values were rounded and adjusted to the figures compiled in Tables 4 and 5. The index “max” indicates that the maximum activity measured in the decay series (^{232}Th, ^{238}U) has to be used for comparison.

The values given correspond to the specific activity (soil) or activity concentration (water) of every single type of nuclide which (under the model assumptions) lead to the doses of 0.1 mSv/a or 0.5 mSv/a, respectively. Because decay-series radionuclides occur always as a mixture, the threshold values can be applied only in connection with the summation formula:

$$\sum \frac{measured\ values}{threshold\ values} < 1 \qquad (9)$$

Table 4: Test thresholds for soil material in assessment step B1 (in connection with summation formula)

Scenario condition		**UBW in Bq/kg**	**OBW in Bq/kg**
Contamination close to or in contact with groundwater	**Th-232**$_{max}$ **U-238**$_{max}$	70 90	350 450
Contamination significantly higher than groundwater	**Th-232**$_{max}$ **U-238** **Ra-226**	15,000 800 300	75,000 4,000 1,500

Table 5Test thresholds for leachate in assessment step B2 (in connection with summation formula)

“n.r.“ = not relevant

	UBW in mBq/l		**OBW in mBq/l**	
Contamination …	close to or in contact with groundwater	significantly higher than groundwater	close to or in contact with groundwater	significantly higher than groundwater
Ra-228	20	1000	90	5,000
Th-228	150	100	600	500
U-238	400	400	2,000	2,000
Ra-226	120	120	600	600
Pb-210	70	n.r.	350	n.r.

As the summation formula is not common practice in soil protection, a simplified assessment was found to be appropriate. Based on the knowledge of the radiological relevance and the typical radionuclide patterns especially in water, new threshold values were derived which roughly conform to the summation formula. These values are shown in Tables 6 and 7.

Soils can be declared uncontaminated as to potential groundwater contamination if the measured specific activities in soil are lower than the "UBW" values in Table 6 *for all nuclides* of the corresponding decay series. There will be a risk of groundwater contamination if the values *of at least one nuclide* are higher than "OBW". Contaminations between "UBW" and "OBW" can be assessed by measuring leached samples (method DIN 38414-4, "S4") and applying Table 7 in the same manner as described before. This enables first assessment by a simple comparison of measuring results and threshold values.

A more detailed user guideline for the threshold values was published by Gellermann et al. /5/.

Table 6 Test thresholds for soil material in assessment step B1 (simplified assessment)

Scenario		**UBW in Bq/kg**	**OBW in Bq/kg**
Contamination close to or in contact with groundwater	**Th-232**$_{max}$ **U-238**$_{max}$	40 40	200 200
Contamination significantly higher than groundwater	**Th-232**$_{max}$ **U-238**$_{max}$	1,000 200	5,000 1,000

Table 7 Test thresholds for leachate in assessment step B2 (simplified assessment)

“n.r.“ = not relevant

	UBW in mBq/l		OBW in mBq/l	
Contamination …	close to or in contact with groundwater	significantly higher than groundwater	close to or in contact with groundwater	significantly higher than groundwater
Ra-228	20	200	60	1,000
Th-228	10	20	50	100
U-238	80	80	400	400
Ra-226	20	20	100	100
Pb-210	20	n.r.	100	n.r.

Background concentrations

Any use of threshold values becomes absurd if the values are too close to background concentrations. In the case presented here, the background values are compared with the “UBW” values in Table 8. The differences are sufficient for distinguishing between contaminated situations and background.

Table 8: Comparison of background values with “UBW” obtained for contaminations close to groundwater

	Soil (sand)		Water	
	Background	**UBW $^{*)}$**	**Background**	**UBW$^{*)}$**
Ra-228	15	40	5	20
Th-228			1	10
U-238	15	40	5	80
Ra-226			8	20
Pb-210			5	20

$^{*)}$ simplified assessment

References

/1/ Ableitung von Prüfwerten für die Beurteilung einer Grundwassergefährdung durch natürlich radioaktive Altlasten. Gutachten HGN Hydrogeologie GmbH, Nov. 2001. Auftraggeber: Landesumweltamt Brandenburg

/2/ Gellermann, R., K. Kip, H. Schulz: Differentiation of radioactive ground contamination with TENORM. Poster presented at Internat. Symposium NORM III, Brussels, 2000.

/3/ Poschner, J. und G. Schaller (1995): Richtwerte für die spezifische Aktivität von schwach radioaktiv kontaminierten Abfällen, die konventionell entsorgt werden. Bericht BfS-ISH-169/95

/4/ Gellermann, R., K. Nindel, J. Schreyer: Mobilisierung und Migration natürlicher Radionuklide – Grundlage für die Expositionspfadanalyse an Standorten der Uran-Bergbausanierung. In: Uranium Mining and Hydrogeology II (Herausg. B. Merkel, C. Helling) Verlag Sven von Loga, Köln 1998, S. 375-382

/5/ Gellermann, R., M. Hahn, U. Haberlau, J. Beetz: Prüfwerte für die Beurteilung der Grundwassergefährdung durch radioaktive Bodenkontaminationen. altlasten spektrum H. 6 (2002) S. 294-302

/6/ Strahlenschutzkriterien für die Nutzung von möglicherweise durch den Uranbergbau beeinflussten Wässern als Trinkwasser. Empfehlung der Strahlenschutzkommission (SSK) vom 10./11.12.1992

NATURAL RADIOISOTOPE LEVEL DIFFERENTIATION IN ARABLE AND NONCULTIVATED SOILS AT ŁĘCZNA-WŁODAWA LAKE DISTRICT

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INTRODUCTION

The Łęczna-Włodawa Lake District (Pojezierze Łęczyńsko-Włodawskie) located on East of Poland is used as recreation ground but mainly it is an agriculture area producing ecological food. This area is relatively low contaminated due to absence of industry. Bogdanka coal mine located 20 km north of Łęczna town at vicinity of Poleski National Park is the only industrial plant. Its activity, despite of the law and technical regulations observance may be disadvantageous for the environment in future. A potential hazard may produce accumulation of natural radioactive elements in soil and bottom sediments, which results from increase of the storage field (up to 83 ha in future) and disposal of coal mine water to the Świnka river [1].

It is also well known that usage of phosphatic and potassic fertilizers introduces additional amounts of the natural radionuclides such as ^{238}U contained in phosphorite and phosphogypsum, and ^{40}K.

The aim of present research was the investigation of activity level and vertical distribution of some natural gamma radioactive isotopes in cultivated soils and comparison of the received results with the ones coming from waste lands samples. Additionally, an attention was paid to the anthropogenic isotope - ^{137}Cs, which being the result of radioactive fallout, may be treated as a marker of the migration rate of isotopes in environment. Valuation of transfer coefficients of some isotopes from soil to selected plants and qualification of purity of soils under studies, in relation to the content of anthropogenic elements was attempted.

The literature data relating to concentration of radioisotopes and their vertical distribution in cultivated soils are not often encountered. Most often waste lands are studied, where isotope migration, being result of natural phenomena (the change of physical, chemical and atmospheric conditions etc.) may be observed [2]. However, for qualification of the possible transfer of contamination from soil to plants and radiochemical purity of soil, the investigations of cultivated terrain is indispensable. In comparison to uncultivated terrain the main difference in a condition of migration is created by mechanical mixing of the surface layer of soil as well as introduction of some radioisotopes with fertilizers as mentioned previously.

MATERIALS AND METHODS

The profile sample of the cultivated soils to 40 cm depth (each layer 5 cm) and surface layer (0-5 cm) of the waste lands were taken in September 2003. Sampling points were selected in vicinity of seven villages of Łęczna-Włodawa Lake District: Świerszczów (marked as *SWI*), Krzczeń *(KRZ)*, Kulczyn *(KUL),* Wola Wereszczyńska *(WOW),* Turno *(TUR),* Ludwin (*LUD*) and Pieszowola (*PIE*). For each of the sample a grain-size distribution as well as content of elements was determined. The soils were qualified as follows: bog soils (*SWI*, *KRZ* and *KUL*), black-earth (*WOW*, *TUR* and *LUD*), and alluvial soil (*PIE*) [3].

To investigate of soil to plant transfer coefficients the samples of vegetables, cultivated on this terrain i.e. beetroot (*beta vulgaris*) and potato (*solanum tuberosum*) as well as their green parts were taken. The measurements of concentration of gamma radioactive isotopes in samples were made spectrometrically with the Silena-Canberra spectrometer equipped with HPGe crystal of active volume 70 cm^3 and relative efficiency 13.5 %.

A quantitative analysis was executed with Genie -2000 computer program (Canberra). All measured results were related to dry weight of samples of soils and plants. A contents of main and trace elements in samples were determined by ED - XRF method with isotope excitation (^{109}Cd) by Canberra spectrometer with Si(Li) detector.

RESULTS AND DISCUSSION

Basing on gamma spectrometric measurements three representative isotopes, being components of natural radioactive series: ^{210}Pb and ^{226}Ra (^{238}U series) as well as ^{212}Pb (^{232}Th series) were chosen for comparison. The concentration of these isotopes in Bq/kg is presented on Figures 1-7 for respective layers of the soil profiles.

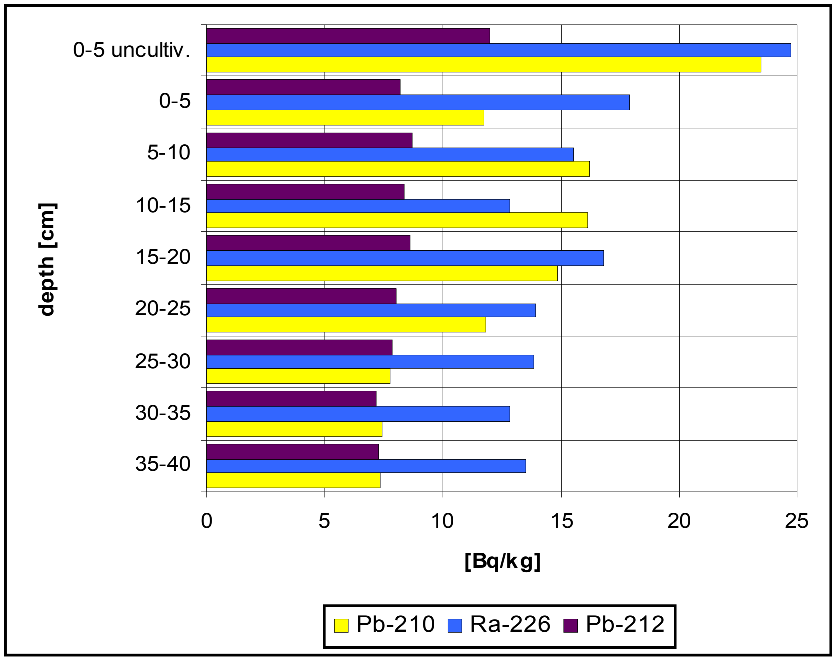

Figure 1. The concentration of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Świerszczów (*SWI*) soil profile.

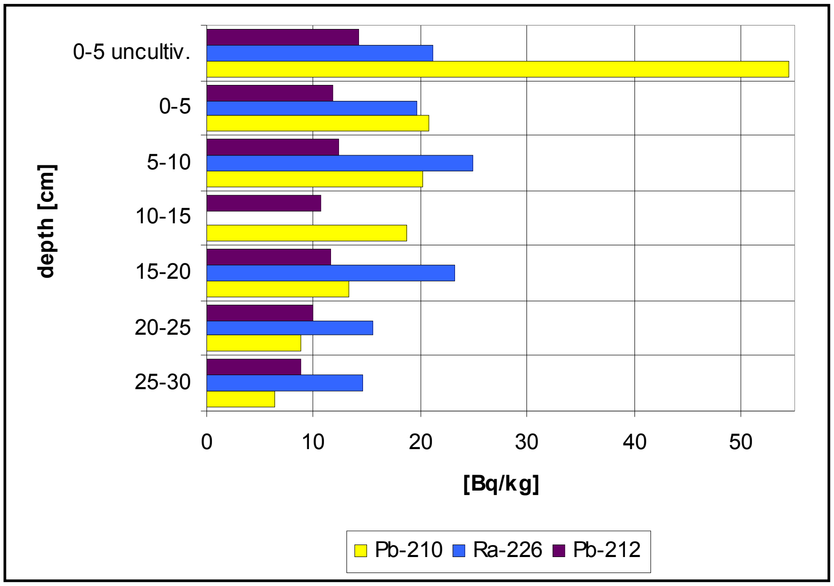

Figure 2. The concentration of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Krzczeń (*KRZ*) soil profile.

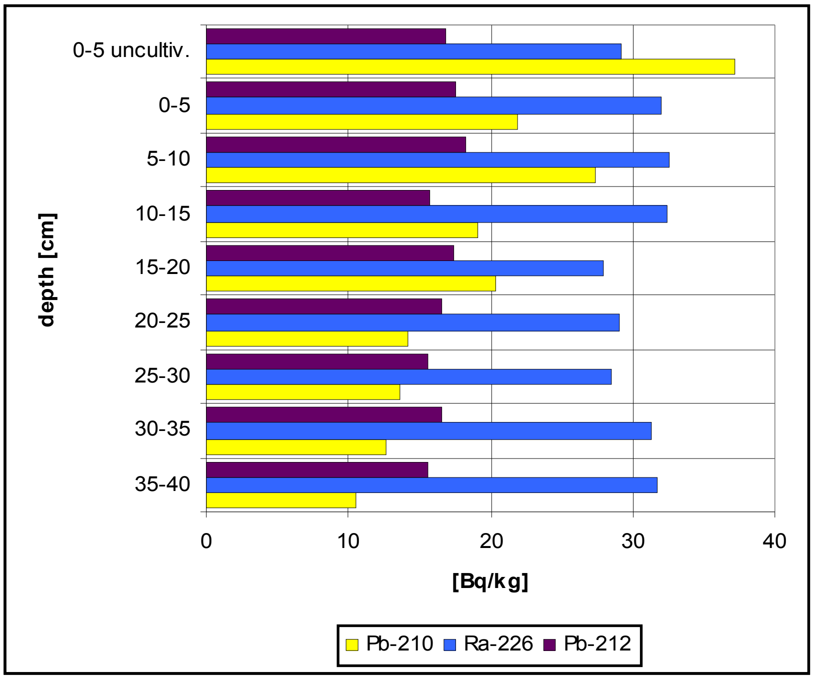

Figure 3. The concentration of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Kulczyn (*KUL*) soil profile.

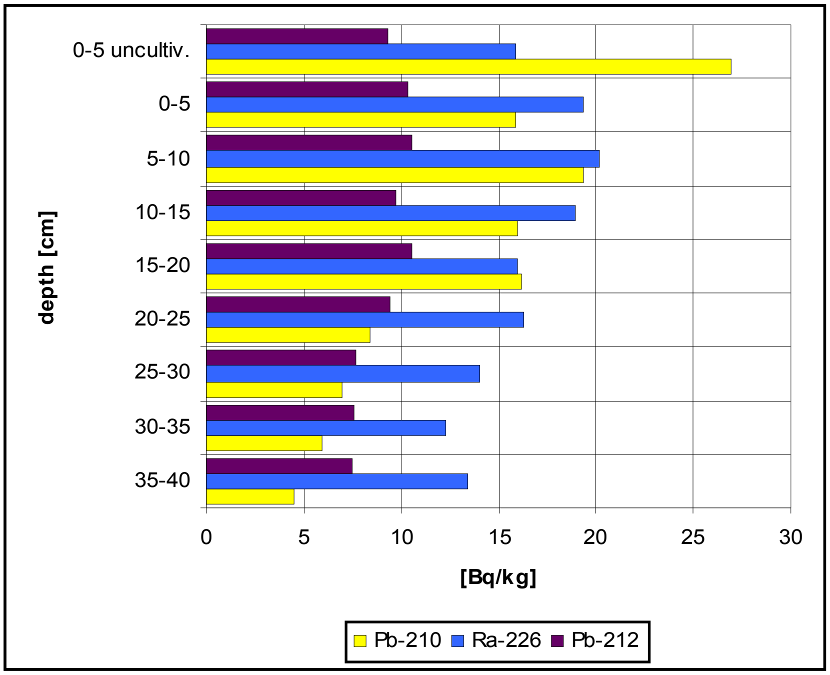

Figure 4. The concentration of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Wola Wereszczyńska (*WOW*) soil profile.

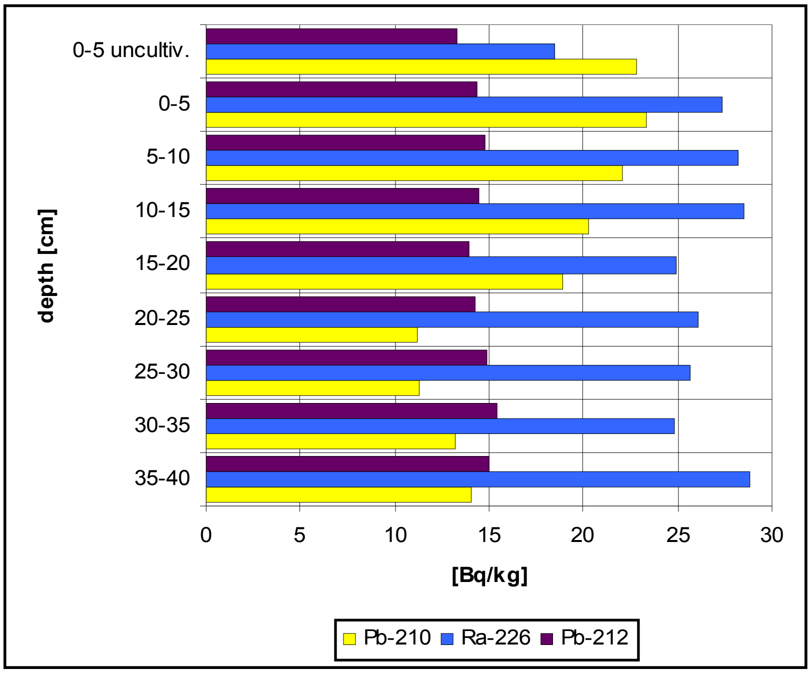

Figure 5. The concentration of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Turno (*TUR*) soil profile.

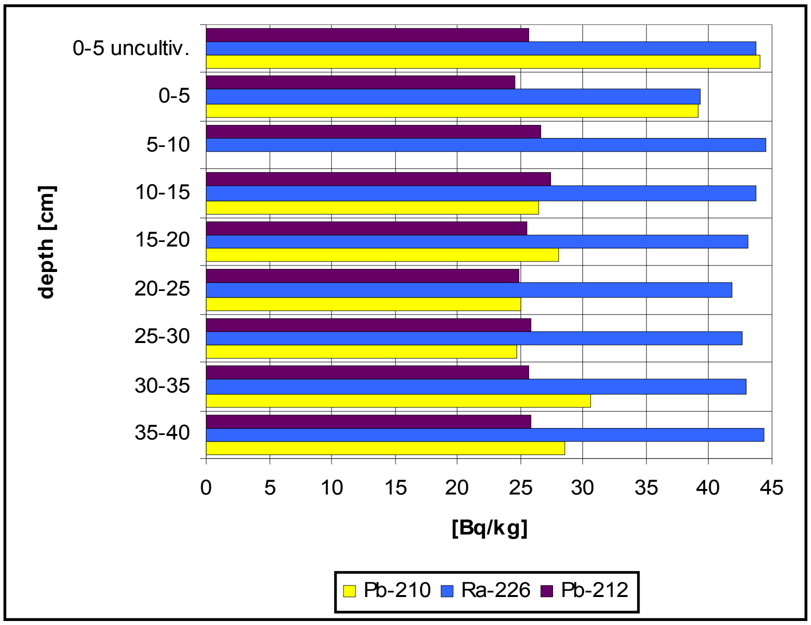

Figure 6. The concentration of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Ludwin (*LUD*) soil profile.

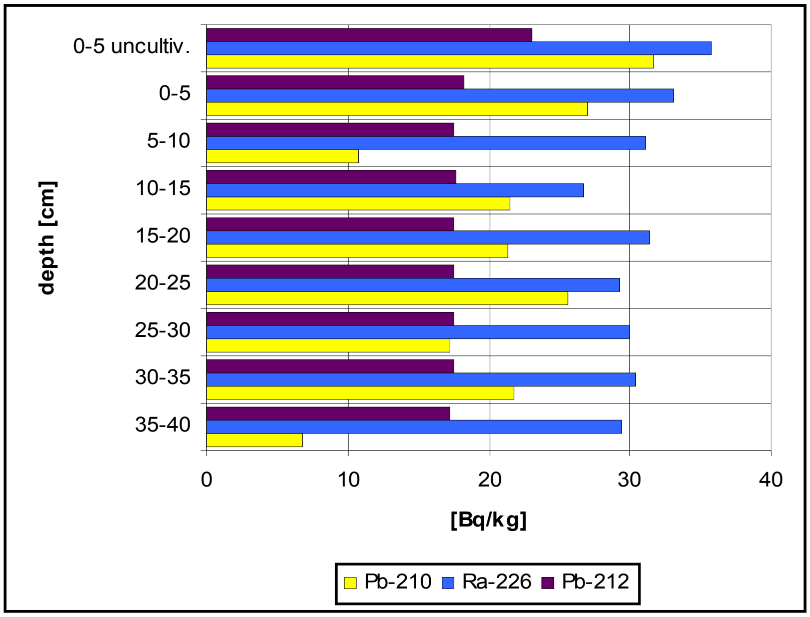

Figure 7. The concentration of ^{210}Pb, ^{226}Ra, and ^{212}Pb in layers of Pieszowola (*PIE*) soil profile.

As can be seen on Figures 1 - 7 the distribution of these natural radionuclides in the soil profiles is even. For comparison the concentration level of the same isotopes in a surface layer of uncultivated terrain was shown. One may state that concentration of ^{210}Pb is higher in uncultivated soil in all cases due to the presence of this isotope in air and their accumulation on the surface of the soil. An intense mixing of the soil during cultivation dilutes this isotope because its concentration in deeper layers is low. In cultivated soil the concentrations of two natural isotopes (^{226}Ra and ^{212}Pb) are the same (*KRZ*, *KUL* and *LUD* samples), lower (*SWI* and *PIE*) or higher (*WOW* and *TUR*) than these in uncultivated layer of the same soil.

One may suppose, that where do not use mineral fertilizers the concentrations of these natural isotopes in cultivated area will be similar or lower in comparison to uncultivated one. Such effect is produced by impoverishment of the soil by crops. Contrary to above, the mineral fertilization will cause the growth of the concentration of the natural radioisotopes in soil. The typical case was met for *WOW* and *TUR* soils.

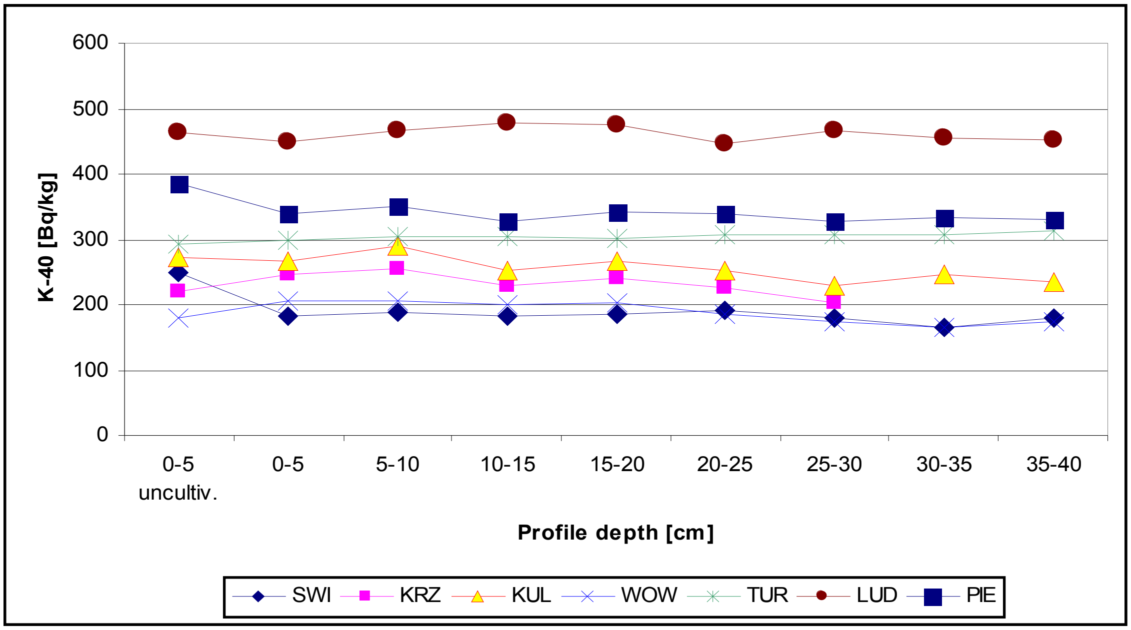

Figure 8. The ^{40}K concentration changes along the depth profile of soils.

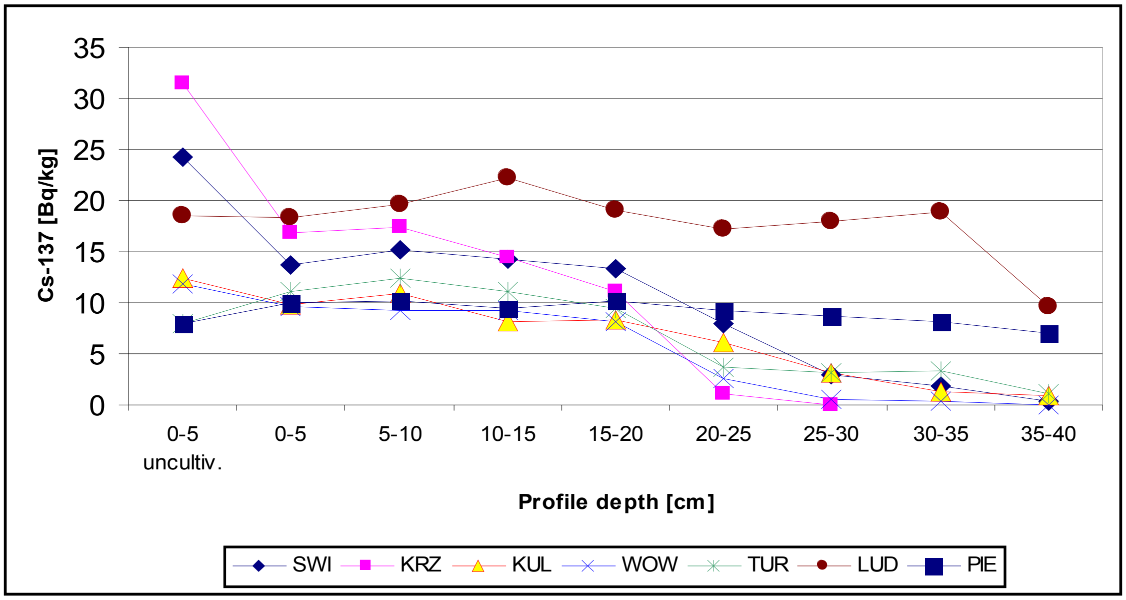

Figure 9. The ^{137}Cs concentration changes along the depth profile of soils.

On separate Figures (Fig. 8 and 9) the concentration changes (Bq/kg) of natural isotope ^{40}K as well as ^{137}Cs, introduced as radioactive fallout, are shown. As can be seen the level of ^{40}K activity is different for samples from various sites, which results from different chemical composition of the respective soils. However, concentration of this isotope does not change meaningfully in the whole studied range of the profile depth of cultivated soil and is similar to values received for uncultivated soils. The ^{137}Cs concentration changes in the profile, shown on Fig. 9, are different from that one observed for the ^{40}K (Fig. 8). The ^{137}Cs appeared as result of radioactive fallout and it migrates downwards from surface layer where its concentration was the largest. In uncultivated soils its concentration diminishes in exponential way with profile depth, achieving the background value at 15 - 30 cm (depending on physicochemical condition, soil composition etc.) [2]. In the case of studied cultivated soils one can observe the same concentration level of ^{137}Cs until to depth ca. 25 cm, then its progressive lowering at 25 - 40 cm depths. The concentration of ^{137}Cs in surface layer (0 - 5 cm) is smaller than that in the same layer of the cultivated soil. Observed equalization of isotope concentrations in layer 0 - 25 cm results from ploughing of the soil and mixing it just to such depth. Samples marked as *LUD* and *PIE* show somewhat different run of cesium concentration changes. The sharp decrease of the cesium concentration in layers 25 - 40 cm was not observed. The most probably it is connected with the presence of relative high concentration of potassium, reaching as much as 2% of dry weight of the soil, as determined by XRF method.

It the next stage of the study the concentration of gamma emitting radioisotopes in samples of beetroot, potato and green parts of these plants was determined. Obtained data were used to calculate of the transfer coefficients (*TF*) of chosen isotopes: ^{210}Pb, ^{214}Pb and ^{226}Ra (^{238}U series), ^{212}Pb (^{232}Th series) as well as ^{40}K and ^{137}Cs. The samples were collected in every sampling place, where soil samples were taken.

The transfer coefficient *TF* was defined as a quotient of the isotope concentration in plant (Bq/kg of dry weight) to its concentration in soil (Bq/kg). The *TF* values of above mentioned isotopes for beetroot, potato tuber and green parts of potato are listed in Table 1 as: arithmetic mean, median, minimum and maximum of measured value.

Table 1. Mean value of transfer coefficients (*TF*) of the chosen isotopes from soil to beetroot, potato tuber and green parts of potato.

		Uranium series			Thorium series		
		^{210}Pb	^{214}Pb	^{226}Ra	^{212}Pb	^{137}Cs	^{40}K
Beetroot	Mean±1σ	0.12±0.10	0.12±0.10		0.03±0.02	0.14±0.09	4.25±1.89
	Median	0.07	0.10		0.01	0.15	3.57
	Minimum	0.05	0.04		0.01	0.02	1.81
	Maximum	0.29	0.32		0.08	0.32	7.25
Potato tuber	Mean±1σ	0.07±0.09	0.18±0.18	0.06±0.03	0.03±0.02	0.07±0.04	2.84±0.84
	Median	0.02	0.10	0.07	0.02	0.07	2.36
	Minimum	0.01	0.04	0.006	0.004	0.02	1.72
	Maximum	0.22	0.60	0.09	0.07	0.16	4.29
Potato green parts	Mean±1σ	2.54±0.55	0.78±0.27	0.29±0.30	0.53±0.14	0.70±0.19	5.22±1.95
	Median	2.61	0.73	0.12	0.59	0.71	5.20
	Minimum	1.88	0.48	0.05	0.32	0.36	2.10
	Maximum	3.61	1.15	0.87	0.69	0.91	7.88

One can notice that *TF* values vary in a large extent. The highest values of ^{40}K in potato and beetroot edible parts confirm accumulation of potassium by plants. Other studied isotopes do not accumulate in edible parts of the studied plants. Considerably higher values of *TF* were calculated for a green, inedible potato parts. In this case, much larger accumulation of ^{40}K than in tuber was observed and also meaningful accumulation of ^{210}Pb. This long-life isotope comes from radon decay and its presence in the green parts results probably from direct sorption from air. The ^{137}Cs comes from radioactive fallout but its concentration in the atmosphere is not significant nowadays. It is transported to green parts of plants by root system because it appears in air as result of soil resuspension only. The TF for ^{137}Cs in green parts is close to unity, which means that cesium concentration in soil is approximately the same.

Analyzing the gamma spectra of the green parts of potato and beetroot the presence of cosmogenic isotope - ^{7}Be of concentration 30 - 90 Bq/kg was stated. This isotope does not exist in soil, and its concentration in surface layer of atmosphere amounted about 3.6 mBq/m^{3} in the year 2003. For this reason one may conclude that presence of ^{7}Be in green parts of plants proves a direct assimilation of this isotope from air by stalks and leaves.

To valuate a level of anthropogenic contamination of the soils the enrichment factor (*EF*) was calculated, defined as follows [4]:

$$EF = \frac{(C_x / C_{Fe})_{in\ sample}}{(C_x / C_{Fe})_{in\ lithosphere}}$$

where: C_x = concentration of given element,
C_{Fe} = concentration of iron.

The concentrations of main and trace elements in soil samples were determined by XRF method. Calculated values of *EF* are shown on Figure 10. For these calculations the mean concentration of respective elements in Earth's crust was applied [6]. The higher than one *EF* coefficient the more pronounced is negative influence of man on the soil.

The *EF* value of all analyzed soils for all studied elements is higher than unit, which proves enrichment of the soil by these elements. An accumulation of some elements in surface soil in comparison to bed-rock is well-known property. Such phenomenon is due to decay of rocks and other soil forming processes. Some elements, such as manganese, strontium, or lead demonstrate higher value of *EF* ranged from 3.5 to 5 [4, 5]. In the case of studied soils, as can be seen on Figure 10, zirconium and lead show relatively high enrichment i.e. mean values of the *EF* equal 32 and 48 respectively. Considering lead, this value is more than ten times higher than expected [4, 5] whereas lack of literature data for zirconium makes the comparison impossible. Two, three times higher values than expected for soils one can observe also in case of copper and zinc, what may be attributed to man's influence on environment.

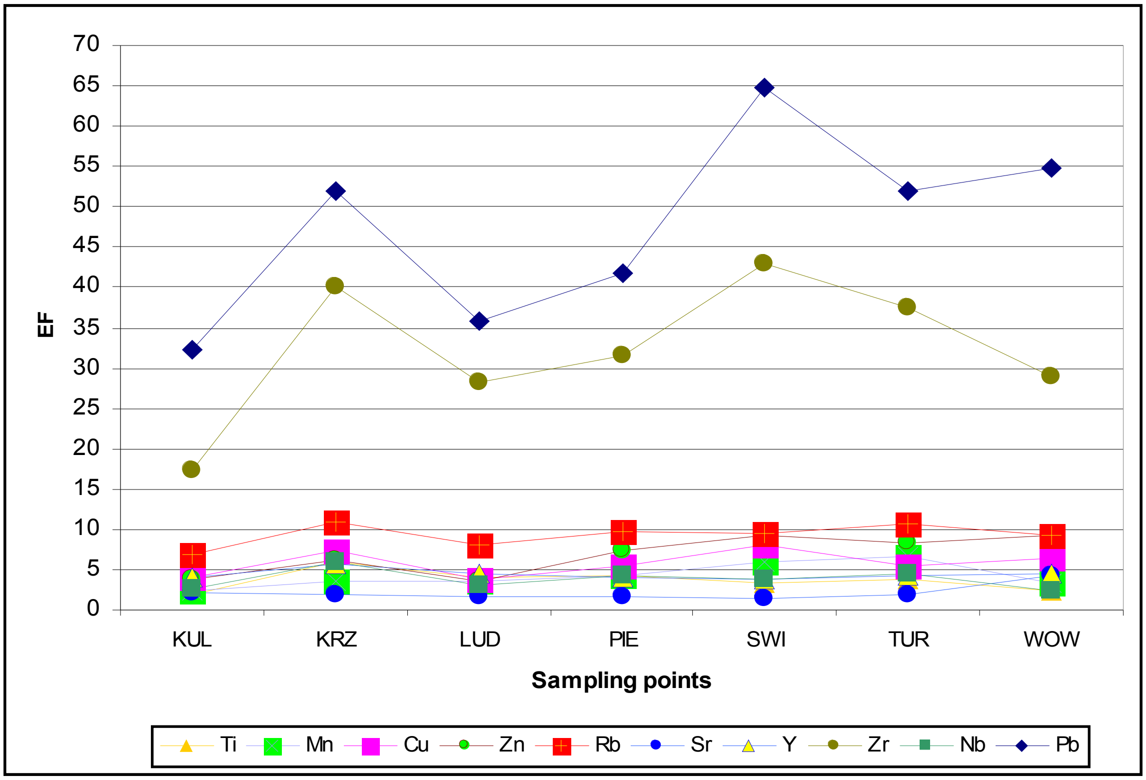

Figure 10. Enrichment factors of the elements in soils.

CONCLUSIONS

Using gamma spectrometry the distribution of the selected radioisotopes of natural series was determined in soil profiles of cultivated soils and compared with uncultivated ones. It was observed, that in the most cases (except two samples) the average concentration of radionuclides in the profile layers is smaller than in surface layer of uncultivated soil, which proves no fertilization at studied terrain. The concentration changes of ^{137}Cs in soil profiles resulted by ploughing of soil to average 25 cm depth and mixing their layers. Calculated soil-to-plant transfer coefficients of studied radionuclides reveal the high concentration of ^{40}K in the edible parts of beetroots and potatoes as well as in their green parts. Relatively high concentration of ^{210}Pb was also found in leaves and stalks of these plants. The XRF method of elemental analysis proved meaningful enrichment of the surface layer of soil with zirconium and lead, as compared with their average content in lithosphere. In a smaller extent the soils were also disadvantageously enriched with copper and zinc.

REFERENCES

1. Biuletyn informacyjny: 25 lat Lubelskiego Zagłębia Węglowego. KWK Bogdanka 2000, s.64.
2. Chibowski St., Komosa A., Reszka M., Solecki J., Zygmunt J., Migration of radionuclides in soils and their accumulation in sediments of superficial waters. IAEA-TECDOC-1314. Radionuclide transport dynamics in freshwater resources. IAEA Vienna 2002, 105-125.

3. Borowiec J., Urban D., Łąki, cz. II. Kondycja geochemiczna siedlisk łąkowych Lubelszczyzny. LTN Lublin, 1997, s.154.
4. Kabata-Pendias A., Pendias H, Biogeochemia pierwiastków śladowych. PWN Warszawa 1993.
5. Kabata-Pendias A., Adriano D. C., Trace metals. Soil Amendments and Environmental Quality (Ed. Rechcigl J. E.), Chapt. 4, CRC Lewis Publ., New York 1995, 139-167.
6. WebElements. Periodic Table (professional edition). www.webelements.com

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PRÓBY OZNACZANIA SZYBKOŚCI EKSHALACJI RADONU ZE SKŁADOWISKA ODPADÓW KOPALNI WĘGLA KAMIENNEGO BOGDANKA PRZY UŻYCIU DETEKTORÓW PICORAD

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WSTĘP

Na terenie Pojezierza Łęczyńsko-Włodawskiego w niewielkiej odległości od obszarów Poleskiego Parku Narodowego (ok. 10 km na wschód od Łęcznej) położona jest kopalnia węgla kamiennego Bogdanka. W pobliżu kopalni od początku jej działalności, tj. przeszło 20 lat, gromadzone są odpady skały płonnej, wydobywanej na powierzchnię wraz z węglem kamiennym. Zaplanowane składowisko obejmuje 83 ha powierzchni. Do chwili obecnej odpady zajęły przeszło 1/3 całej powierzchni składowiska tworząc hałdę o wysokości ok. 25 m. Północno- i południowo-zachodnie zbocze hałdy zostało umocnione, przysypane warstwą ziemi o niewielkiej grubości i obsadzone krzewami. Odpady kopalniane tworzą głównie łupki ilaste, stanowiące ok. 88%, a na pozostałe 12% składają się: piaskowce, syderyty i mułowce [1]. Składowiska odpadów mogą być źródłem radonu. Składowany materiał wykazuje zwykle podwyższone stężenie ^{226}Ra [2]. Obszary takie mogą stanowić zagrożenie i zgodnie z tendencjami panującymi w ochronie radiologicznej [3] powinny być monitorowane. Szybkość uwalniania radonu za składowiska zależy od bardzo wielu czynników, dlatego też najbardziej wiarygodne dla oceny szybkości ekshalacji radonu są bezpośrednie pomiary.

Celem pracy są próby zastosowania detektorów Picorad (Niton, Canberra) do badania ekshalacji radonu ze składowiska odpadów kopalni Bogdanka. Detektory Picorad, zawierające aktywowany węgiel oraz niewielką ilość substancji pochłaniającej wilgoć należą do grupy detektorów pasywnych. Ich działanie polega na sorpcji radonu z powietrza (najczęściej przez 48 godzin) i pomiarze aktywności radonu i produktów jego rozpadu po ich desorpcji do ciekłego scyntylatora. Detektory te są przeznaczone w zasadzie do detekcji radonu w pomieszczeniach o stałej jego koncentracji. W przypadku użycia tych detektorów do pomiarów na odkrytym terenie pojawia się problem wysokiej wilgotności i zmiennego, narastającego stężenia radonu wydzielającego się z materiału skalnego.

METODYKA BADAŃ

Punkty pomiarowe ekshalacji radonu wybrano w okolicach szczytu hałdy na obszarze częściowo zrekultywowanym i na odkrytej skale płonnej na szczycie. Miejsce poboru próbek opisują współrzędne geograficzne: 51˚19'01 N i 22˚59'38 E. W 12 punktach, z których skrajne były odległe od siebie o ok. 100m, umieszczono naczynka Picorad, które przykryto miskami stalowymi o objętości 2,5dm^3 i średnicy 25cm. Pomiar odbył się w styczniu 2004, gdy hałda była pokryta niewielką warstwą śniegu. Miski zostały umieszczone tak, aby dokładnie przylegały do odsłoniętej warstwy gleby lub skały, a następnie zostały uszczelnione śniegiem lub materiałem skalnym. Pomiar wydzielającego się radonu prowadzono przez 3 godziny przy temperaturze powietrza -5˚C, wilgotności względnej ok. 75% i ciśnieniu 995 hPa. Po tym czasie naczynka zostały przewiezione do laboratorium, gdzie po ok. 1 godz. od zakończenia pomiaru poddano je normalnej procedurze analitycznej. Zastosowano scyntylator Instafluor (Packard) oraz spektrometr Quantulus 1220-002 (Wallac-Perkin-Elmer) do pomiaru promieniowania emitowanego przez radon i produkty jego rozpadu w zakresie kanałów 466 – 902 w konfiguracji wysokoenergetycznego promieniowania beta bez stosowania opcji zmniejszających tło. Otrzymane wyniki w postaci szybkości zliczania (impulsy na minutę) przeliczono przy pomocy programu komputerowego Picorad 5.9 (Niton) na wielkość stężenia radonu (Bq/m^3).

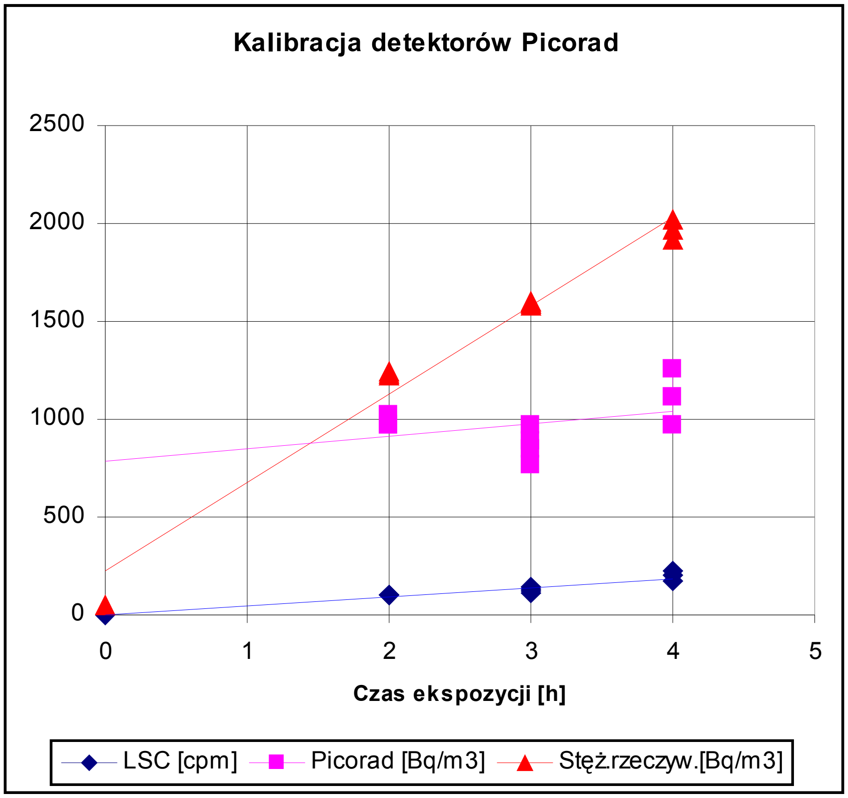
Program obliczający stężenie radonu w powietrzu na podstawie pomiaru szybkości zliczania zakłada co najmniej 12 godzinną sorpcję radonu z powietrza przy niewiele zmieniającym się poziomie jego aktywności. W przypadku krótszych czasów ekspozycji i narastającej aktywności zastosowanie programu przeliczeniowego może być ograniczone. Dlatego też przeprowadzono odpowiednią kalibrację detektorów Picorad w komorze radonowej Laboratorium Radiometrii GIG w sposób opisany poniżej.

Komorę o objętości 7,25 m^3 przewietrzono w celu obniżenia stężenia radonu do poziomu jak na otwartym powietrzu. Bezpośrednio przed rozpoczęciem ekspozycji przez źródło przepływowe typu Ra-1025 firmy PYLON przepompowywano powietrze przez około 15 minut w celu usunięcia radonu ze źródła. Do przewietrzonej komory wstawiono detektory Picorad, detektory węglowe GIG oraz źródło radonowe zaopatrzone w pompkę do ciągłego przepompowywania przez nie powietrza. Po zamknięciu komory rozpoczęto ekspozycję, która trwała 4 godziny. Po 2 i 3 godzinach wyjęto część detektorów oraz pobrano próbki do dwu komór Lucasa w celu określenia stężenia radonu w komorze radonowej po tym czasie. Detektory Picorad zostały zanalizowane po przewiezieniu do Lublina, po ok. 24 godz. od chwili zamknięcia.

WYNIKI I DYSKUSJA

I. Kalibracja detektorów Picorad.

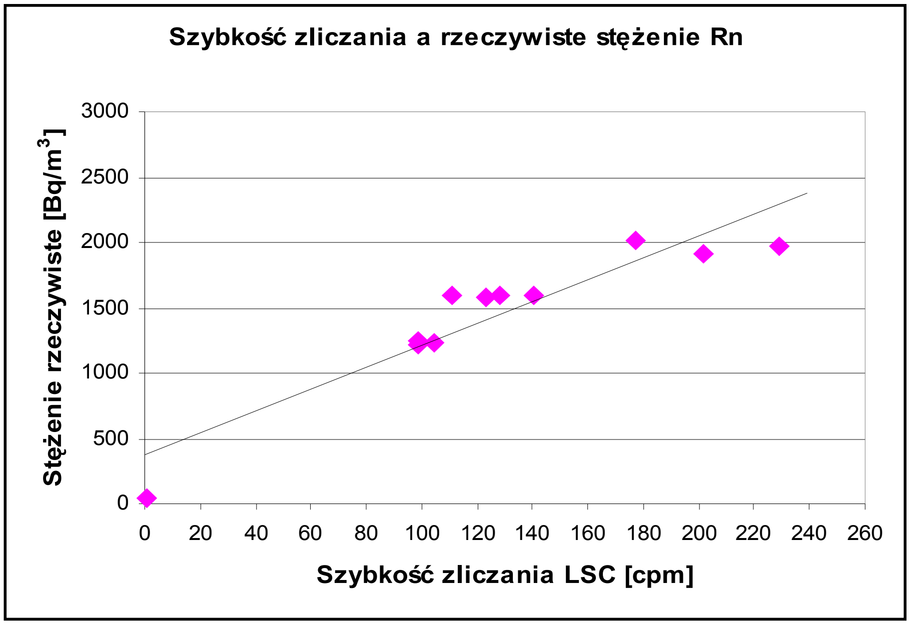
Wyniki przeprowadzonej w komorze radonowej kalibracji detektorów Picorad przedstawia rysunek 1. Pokazuje on zależność od czasu rzeczywistego stężenia radonu panującego w komorze [Bq/m^3] (oznaczonego metodą skalibrowanych detektorów węglowych oraz komór Lucasa), zmierzonej wielkości szybkości zliczania impulsów w detektorach Picorad [cpm] oraz obliczonego na ich podstawie, przy pomocy programu komputerowego Picorad 5.9, stężenia radonu [Bq/m^3].



Rys.1. Kalibracja detektorów Picorad. Zmiany z czasem ekspozycji rzeczywistego stężenia radonu w komorze, szybkości zliczania w ciekłym scyntylatorze i obliczonego na podstawie pomiarów radiometrycznych stężenia radonu wykazywanego przez detektory Picorad.

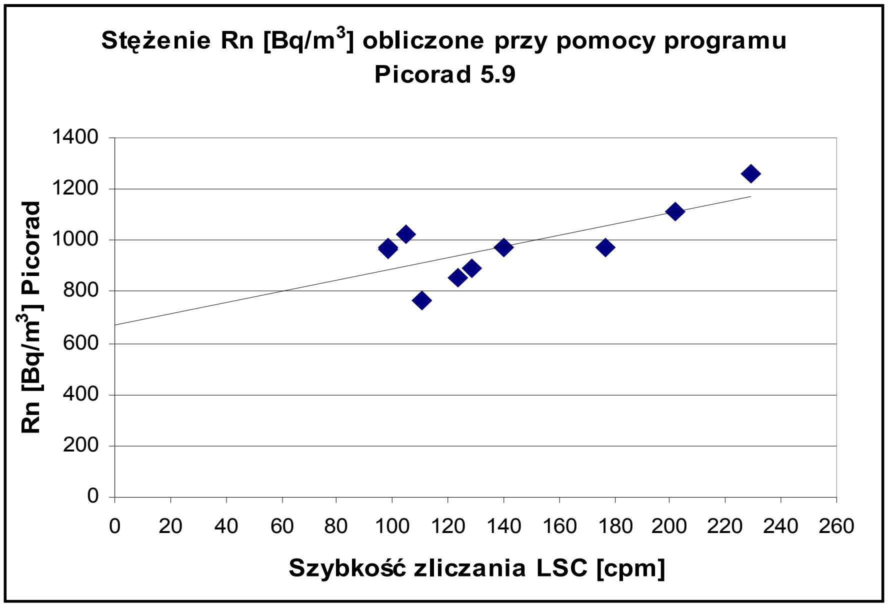
Jak można zaobserwować rzeczywiste stężenie radonu w komorze wzrastało liniowo z czasem o ok. 450 $Bq \cdot m^{-3} \cdot h^{-1}$. Korelacja liniowa punktów opisana współczynnikiem Pearsona wynosi 0,986. Podobnie liniowo wzrasta szybkość zliczania mierzona przy pomocy spektrometru z ciekłym scyntylatorem w detektorze Picorad. Punkty pomiarowe układają się na prostej, a współczynnik korelacji jest również wysoki i wynosi 0,952. Natomiast stężenia radonu obliczone na podstawie szybkości zliczania przy pomocy programu Picorad 5.9 wyraźnie odbiegają od przebiegu liniowego:

można zaobserwować zbyt wysokie wartości otrzymane po 2 godzinach ekspozycji. Przyczyną tego jest prawdopodobnie zbyt krótki czas ekspozycji, co prowadzi do błędnych wyników obliczeń. Aby lepiej zaobserwować zależność szybkości zliczania i rzeczywistego stężenia radonu oraz obliczonego programem Picorad 5.9 wykonano rysunki 2 i 3.



Rys.2 Rzeczywiste stężenie radonu w komorze w zależności od szybkości zliczania w ciekłym scyntylatorze detektorów Picorad.

Przedstawiona na rysunku 2 zależność rzeczywistego stężenia radonu w komorze od szybkości zliczania impulsów w ciekłym scyntylatorze (detektory Picorad) dość dobrze spełnia zależność liniową. Współczynnik korelacji Pearsona wynosi 0,87. Natomiast stężenie radonu obliczone programem Picorad 5.9 wykazuje gorszą korelację z szybkością zliczania w ciekłym scyntylatorze, wynoszącą 0,73. Od przebiegu liniowego wyraźnie odbiegają punkty pomiarowe otrzymane po najkrótszym czasie ekspozycji, tj. 2 godzinach. Ich usunięcie poprawia korelację do wartości 0,93.



Rys. 3.Obliczone programem Picorad 5.9 stężenie radonu w zależności od szybkości zliczania w ciekłym scyntylatorze.

Analiza powyższych zależności pozwala stwierdzić, że rzeczywiste stężenie radonu w komorze jest lepiej skorelowane w badanym zakresie z szybkością zliczania w ciekłym scyntylatorze, może być więc lepszym wskaźnikiem stężenia radonu niż stężenie obliczone programem Picorad 5.9.

II. Wyniki pomiarów ekshalacji radonu ze składowiska odpadów.

Wyniki 3-godzinnych pomiarów ekshalacji radonu przedstawia tabela 1. Przedstawiono szybkość zliczania w ciekłym scyntylatorze impulsów w detektorze Picorad, aktywność radonu i produktów rozpadu obliczoną przy założeniu 100% wydajności pomiaru oraz współczynnik ekshalacji radonu zdefiniowany następującym równaniem [4]:

$$\varphi_{Rn} = \frac{A_{Rn}}{S \cdot t} \qquad (1)$$

gdzie: φ_{Rn} = współczynnik ekshalacji radonu [$Bq \cdot m^{-2} \cdot s^{-1}$],

A_{Rn} = aktywność radonu [Bq],

S = powierzchnia ekshalacji [m^2],

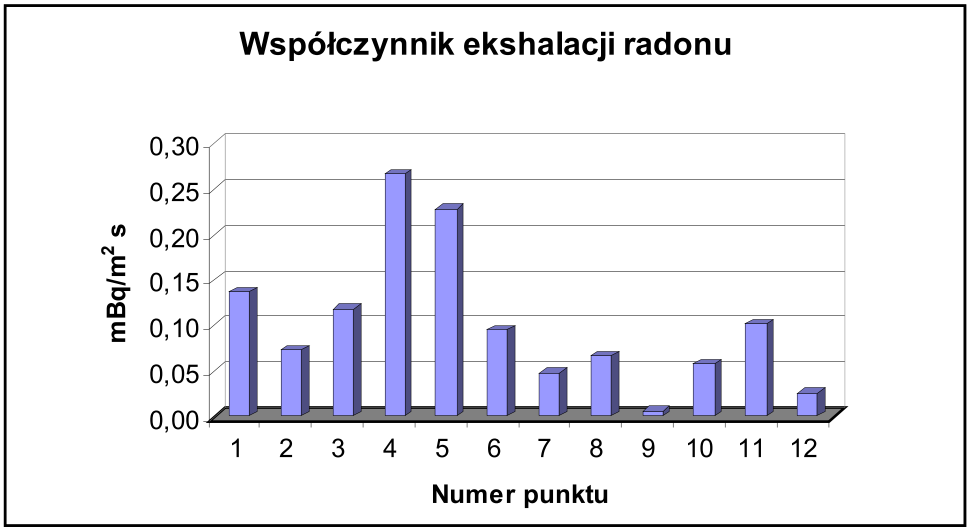
t = czas kumulacji radonu [s].

Tabela 1. Wyniki pomiarów ekshalacji radonu.

	Szybkość zliczania LSC Picorad - tło [cpm]	Aktywność [mBq]	Współczynnik ekshalacji [$mBq \cdot m^{-2} \cdot s^{-1}$]
Powierzchnia zrekultywowana	4,34	72,3	0,136
	2,32	38,7	0,073
	3,74	62,3	0,118
	8,48	141,3	0,267
	7,27	121,1	0,229
	3,03	50,5	0,095
	1,51	25,2	0,047
Powierzchnia świeżej skały	2,12	35,3	0,067
	0,20	3,33	0,006
	1,82	30,3	0,057
	3,23	53,8	0,102
	0,81	13,5	0,025

Obliczone współczynniki ekshalacji radonu okazały się małe w porównaniu z danymi literaturowymi, które zawierają się w granicach od kilku do kilkudziesięciu $Bq \cdot m^{-2} \cdot s^{-1}$

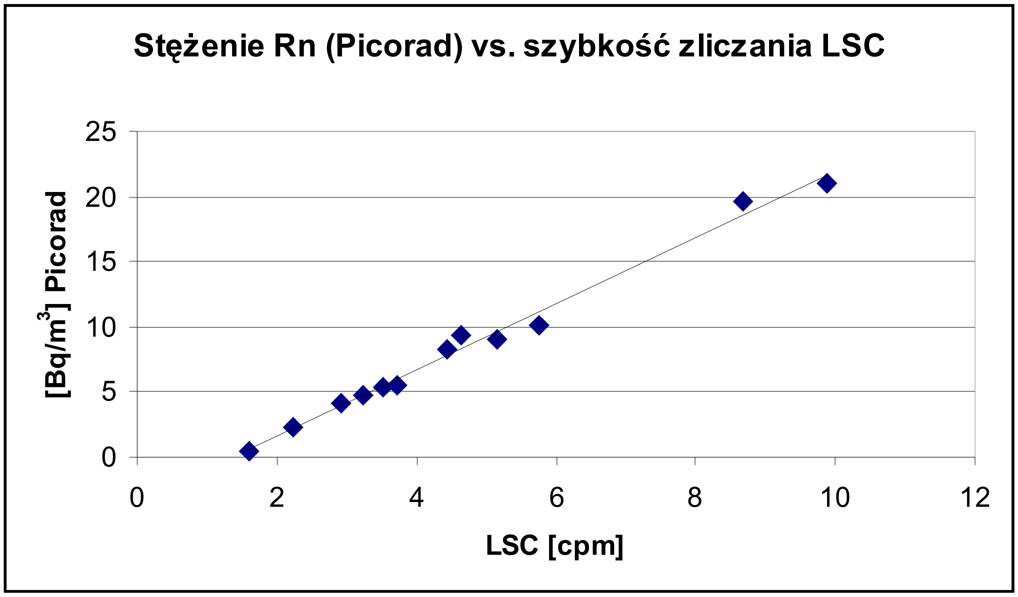
[4]. Jednak trzeba pamiętać, że badania wykonano w zimie, przy temperaturze powietrza -5˚C utrzymującej się na tym poziomie od jakiegoś czasu. Gleba była więc zmarznięta, co powodowało utrudnienie dyfuzji radonu. Pomiary te zostaną powtórzone w innych warunkach atmosferycznych w najbliższym czasie. Wielkości współczynników ekshalacji radonu podano na rysunku 4 dla poszczególnych punktów pomiarowych. Punkty od 1 do 7 odpowiadają powierzchni zrekultywowanej, pozostałe – powierzchni świeżej skały płonnej.



Rys. 4. Wielkość współczynnika ekshalacji radonu z powierzchni hałdy.

Analizując dane z tabeli 1 oraz rysunku 4 można zaobserwować, że średnie wartości współczynnika ekshalacji radonu z powierzchni zrekultywowanej są ok. 2,5-krotnie większe niż ze świeżej skały. Odpowiednie wartości wynoszą: 0,138±0,075 $\mathrm{mBq\cdot m^{-2}\cdot s^{-1}}$ i 0,051±0,033 $\mathrm{mBq\cdot m^{-2}\cdot s^{-1}}$. Wytłumaczeniem tego zjawiska może być wspomniany fakt zmarznięcia gleby wpływający na wielkość ekshalacji oraz niedostatecznego uszczelnienia brzegów miski, zwłaszcza na obszarach występowania świeżej skały, często w postaci dużych, nierównych odłamków.

Na podstawie wyników pomiarów szybkości zliczania obliczono średnie stężenie radonu, jakie podaje program Picorad 5.9. Wyniki te przedstawiono na rysunku 5 w postaci wykresu zależności obliczonego stężenia radonu od szybkości zliczania. Zależność ta charakteryzuje się dobrym dopasowaniem do równania prostej, a współczynnik korelacji Pearsona wynosi 0,99. Ponieważ pomiary sorpcji radonu prowadzono przez 3 godziny, można stwierdzić, że taki czas sorpcji jest wystarczający dla otrzymania wiarygodnych wyników przeliczenia szybkości zliczania na stężenie programem Picorad 5.9.



Rys. 5. Zależność obliczonego programem Picorad 5.9 stężenia radonu [Bq/m^3] od szybkości zliczania impulsów w ciekłym scyntylatorze [cpm].

Dodatkowo, aby potwierdzić otrzymane wyniki przeprowadzono pomiary zawartości ^{226}Ra w próbkach skały płonnej pobranej wcześniej z różnych miejsc hałdy. Zastosowanie spektrometrii promieniowania gamma z detektorem germanowym pozwoliło na określenie średniej zawartości tego izotopu na poziomie 60 Bq/kg.

Współczynnik ekshalacji radonu φ_{Rn} związany jest z zawartością radu w materiale następującym równaniem [5,6]:

$$\varphi_{Rn} = \varepsilon \cdot A_{Ra} \cdot \rho \cdot \lambda_{Rn} \cdot R \cdot f \qquad (2)$$

gdzie: ε = współczynnik emanacji,

A_{Ra} = stężenie radu w glebie [Bq/kg],
ρ = gęstość gleby [kg/m^3],
λ_{Rn} = stała rozpadu promieniotwórczego radonu = $2{,}0974 \cdot 10^{-6}$ s^{-1},
R = długość dyfuzji [m],
f = czynnik porowatości uwzględniający wilgotność gleby.

Droga dyfuzji R zależna jest od współczynnika dyfuzji w następujący sposób [5,6]:

$$R = \frac{\sqrt{D}}{\sqrt{\lambda_{Rn}}} \qquad (3)$$

gdzie: D = współczynnik dyfuzji radonu w glebie [m^2·s^{-1}],

Biorąc pod uwagę przedstawione w tabeli 1 wartości współczynników ekshalacji otrzymane z przeprowadzonych pomiarów oraz równanie (2) można obliczyć wartość drogi dyfuzji, przyjmując racjonalne wartości pozostałych parametrów. Pozwoli to w następnym etapie, na podstawie równania (3), oszacować wartość współczynnika dyfuzji radonu w danych warunkach. Przyjęto więc wartość współczynnika emanacji ε równą 0,2 oraz czynnika porowatości równą 0,4 [5] Pozostałe czynniki, tj. stężenie radu i gęstość materiału zostały wyznaczone doświadczalnie. Obliczoną w powyższy sposób średnią drogę dyfuzji radonu *R* oraz odpowiadający jej współczynnik dyfuzji *D* podaje tabela 2.

Tabela 2. Średnia droga dyfuzji radonu i współczynniki dyfuzji.

	R [cm]	D [$m^2 \cdot s^{-1}$]
Powierzchnia zrekultywowana	1,0	$2{,}6 \cdot 10^{-10}$
Powierzchnia świeżej skały	0,4	$4{,}0 \cdot 10^{-11}$

Otrzymane wartości są dużo mniejsze niż spodziewane dla gleb w normalnych warunkach, a odpowiadają raczej takim materiałom jak lite skały (marmur, granit, piaskowiec), czy materiały budowlane (beton) [6,7]. Potwierdza to wcześniejszy wniosek, że w badanych warunkach dyfuzja radonu była w dużym stopniu ograniczona, co zmniejszyło w dużym stopniu szybkość ekshalacji. Za różnice w wartościach R na powierzchniach zrekultywowanych i świeżych odpowiedzialna jest najprawdopodobniej różna porowatość tych materiałów (opisywana czynnikiem f) oraz różna wartość zdolności emanacyjnej (jaką opisuje współczynnik ε). Dla tych dwu współczynników przyjęto, podane powyżej, stałe wartości.

WNIOSKI

Wykazano możliwość zastosowania detektorów Picorad do badania ekshalacji radonu ze składowiska odpadów kopalni Bogdanka. Przeprowadzona kalibracja detektorów Picorad w komorze radonowej pozwoliła na stwierdzenie, że minimalny czas ekspozycji detektorów, pozwalający na zastosowanie programu komputerowego Picorad 5.9 do obliczenia stężenia radonu wynosi 3 godziny. Znajomość stężenia radu w badanym materiale podłoża oraz obliczonej szybkości ekshalacji radonu pozwoliło na oszacowanie średniej drogi dyfuzji radonu w skale płonnej z kopalni Bogdanka. Średnia długość drogi wyniosła ok. 1 cm na powierzchni zrekultywowanej oraz 0,4 cm na powierzchni świeżej skały płonnej. Odpowiadające tym wartościom współczynniki dyfuzji radonu wynosiły: $2{,}6\cdot10^{-10}$ $m^2\cdot s^{-1}$ oraz $4{,}0\cdot10^{-11}$ $m^2\cdot s^{-1}$. Wartości te są zbliżone do obserwowanych dla materiałów o małej przepuszczalności, jakimi są lite skały.

ACKNOWLEDGEMENT

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LITERATURA

1. Biul etyn informacyjny: 25 lat Lubelskiego Zagłębia Węglowego. KWK Bogdanka 2000, s.64.
2. Chałupnik St., Kopalnie jako źródło skażeń promieniotwórczych środowiska. Materiały Konf. Naukowo-Szkoleniowej Naturalna promieniotwórczość w środowisku. Prace Naukowe GIG, Katowice 1996, 131-143.
3. Directive 96/29 Euratom on the Basic Safety Standards for the Protection of Workers and the General Public against Ionising Radiation. Official Journal, European Communities, L 159, 1996.

4. Chałupnik St., Wysocka M., Pomiary ekshalacji radonu z gruntu – opracowanie metodyki i wyniki wstępne. Prace Naukowe GIG. Górnictwo i Środowisko, 1 (2003) 61-72.

5. Nazaroff W. W., Radon transport from soil to air. Rev. Geophys., 30 (1992) 137-160.

6. Keller G., Hoffman B., Feigenspan T., Radon permeability and radon exhalation of building materials. Sci. Total Environ., 272 (2001) 85-89.

7.Carrera G., Garavaglia M., Magnoni S., Valli G., Vecchi R., Natural radioactivity and radon exhalation in stony materials. J. Environ. Radioactivity, 34 (1997) 149-159.

APPLICATION OF LIQUID SCINTILLATION COUNTING TECHNIQUES TO GROSS ALPHA, GROSS BETA, RADON AND RADIUM MEASUREMENT IN PORTUGUESE WATERS

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Abstract

Natural waters may contain a number of alpha and beta emitters and the routine control of the drinking water quality requires measuring mixtures of naturally occurring and artificial α and β emitters. The Portuguese law has adopted radioactivity limit values of 0.1 Bq l^{-1} and 1 Bq l^{-1} for gross alpha and gross beta activities, respectively.

The main goal of this work was to develop, to test and to optimise new radiometric techniques for measuring mixtures of α and β emitters in drinking waters. The liquid scintillation counting technique has been optimized for the determination of these radiological parameters. A low background liquid scintillation system with the ability to discriminate between alpha and beta particles by pulse shape analysis (PSA) was used. High counting efficiencies and very low limits of detection were obtained through optimising the pulse shape discrimination and careful selection of scintillation cocktails. The first studies on the radioactivity content of some bottled waters and drinking water from public supplies showed that the limits were not exceeded in general. Radon concentrations in water could also be determined through direct measurement of ^{222}Rn short lived daughter products using the liquid scintillation counting technique. The counting efficiency was closer to the theoretical maximum expected, i. e. 500%. The LLD value for radon measurements in water was 0.195 Bq l^{-1} using a counting time of 60 min. The technique was also tested for the determination of ^{226}Ra in natural waters, and results are shown for gross alpha, gross beta, ^{222}Rn and ^{226}Ra measurements in drinking waters and pond waters in old open pit uranium mines.

Introduction

The Portuguese Law[1] on quality of the water for human consumption adopted limit values of 0.1 Bq l^{-1} and 1 Bq l^{-1} for gross alpha and gross beta activities, respectively. Radon (^{222}Rn) concentration in drinking water is not regulated in Portugal. However, an European Recommendation[2] on the radiological quality of drinking water sets guidelines on radon and long lived radon decay products. For water supplied as part of a commercial or public activity, if the concentration for radon exceeds 100 Bq l^{-1} the Member States should set a reference level for radon to be used for consideration whether remedial action is needed to protect human health. A level higher than 100 Bq l^{-1} may be adopted if national surveys show that this is necessary for implementing a pratical radon programme.

The gross alpha and beta activities measured in drinking waters from public water supplies during the previous years were, in general, lower than the limits recently adopted in the Portuguese Law.[3, 4] However, some water samples collected in granite regions did show activity values higher than the recommended limits.[5] Therefore the periodic analysis of radioactivity in the water for human consumption is of great importance to ensure the radiological quality of water to the population.

One of the most practical methods for determination of gross alpha, gross beta and ^{222}Rn in water is based on Liquid Scintillation Counting (LSC). LSC has been widely used in the area of radiological analyses of environmental samples. This method has several advantages over the more conventional counting methods.[6, 7] The liquid scintillation technique combines the advantages of minimal sample preparation time, small sample size, reduced counting time, high sensitivity and detection efficiency closer to 100%. For the determination of gross alpha/ beta activities by LSC technique there is no self-absorption problem like the one observed in the conventional analytical method where the sample is evaporated to dryness on a planchet and the radiation emitted by the residue measured in a counter.[8, 9]

The LSC technique became also widely used for measuring radon.[10, 11, 12, 13] Radon is highly soluble in toluene and in other organic solvents frequently used in the preparation of scintillation cocktails. In a closed vial, the ^{222}Rn is extracted from the water phase into the organic phase of the scintillation cocktail.

In this work it is tested the use of a very low background liquid scintillation system with pulse shape analysis to determine gross alpha, gross beta and radon, as well as dissolved radium in drinking water at low concentration levels.

2. Materials and Methods

2.1. Equipment and radioactive standards

For gross alpha, gross beta and radon measurements in water samples a low-level Tri-Carb 3170 TR/SL (Packard) equipment was used. The counter has a Bismuth Germanium Oxide (BGO) guard detector, that completely surrounds the sample vial and delivers a background lower than in common counters. Typically, background counts in the 0-1000 keV region range from 2-4 cpm for alpha particles and 11-16 cpm for beta emitters. This counter has the ability to discriminate between alpha and beta particles by pulse-shape discrimination (PSD) based on pulse-shape analysis (PSA). To optimize the discriminator setting two standard sealed vial sources of ^{241}Am and ^{36}Cl (Packard), with 50000 dpm each, were counted. The efficiency counting for gross alpha/beta and radon measurements was determined with standard source solutions of ^{241}Am, ^{90}Sr and ^{226}Ra purchased from Amersham. Sets of standards with various radionuclide concentrations were prepared from these solutions, diluting a few microlitres of the source solution with 10 ml of distilled water and mix with 10 ml of cocktail in 22 ml glass scintillation vials (Packard). The Ultima Gold AB cocktail (Packard) was used in the preparation of ^{241}Am and ^{90}Sr sources and the Opti-Fluor-O (Packard) in the preparation of ^{226}Ra standards. The background vials were prepared with distilled water using the same 10:10 volume ratio.

2.2. Determination of gross alpha/beta

Water samples (1000 ml) were acidified with 1 ml HCl[&] to avoid losses due salt precipitation in the glass beakers with heating. Samples were pre-concentrated by slow evaporation on a hot plate to improve the detection limits. Usually, in acidified water the reduction of sample volume by a factor of 10 is sufficient to obtain samples with measurable activities without the formation of precipitates and without losses of volatile activity.[8] One aliquot of 10 ml of this aqueous concentrate was withdrawn and added to 10 ml of cocktail (Ultima Gold AB, Packard) in 22 ml glass scintillation vial (Packard). With this cocktail and with this sample:scintillator volume ratio at 20ºC, the sample is entirely soluble in the LSC cocktail and does not exceed the holding capacity of the cocktail. According to the manufacturer Ultima Gold AB cocktail is a safe cocktail designed specifically to hold large volumes of acid aqueous solutions with excellent alpha/beta separation performance.[15] The counting time for each sample was 240 minutes. Detection efficiency was evaluated through measuring ^{241}Am and ^{90}Sr/ ^{90}Y standards prepared in laboratory.

2.3. Determination of radon and radium

Prior to sample collection, 10 ml of an non aqueous liquid scintillation solution, Opti-Fluor-O (Packard) was added to a 22 ml glass scintillation vial[¥] and tightly closed with a poly-cone cap. The vials containing scintillation fluid were weighted. In the field, 10 ml[§] water samples were taken with a plastic syringe and the water gently injected below the surface of the cocktail to avoid degassing of ^{222}Rn from the sample to the atmosphere. The vial was tightly closed again and the time of sample collection

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[&] Nitric acid was avoided because it reacts with the cocktail Ultima Gold AB[14]
[¥] Rn diffuses through polyethylene and losses may occur[16]
[§] Better performance was obtained in the 10:10 sample: cocktail than with other volume configurations[17]

recorded. The vials were taken to the laboratory for counting ^{222}Rn activity as soon as possible. The sample vials were reweighted to determine more accurately the mass of the sample and hence the volume, assuming unit density for water. Radon background vials were prepared using the same method as for drinking water samples. A waiting period of at least 3 h was always allowed between the collection and the measurement of the sample radioactivity, in order to ensure the formation of radioactive equilibrium between ^{222}Rn and ^{222}Rn short-lived decay products. Measurements were carried out at 20 ºC using a counting time for each sample of 60 minutes. The net count rate of every sample vial was corrected for the radioactive decay of radon between the time of sample collection and radioactivity counting.

The same sample was measured again after 30 days later. At this time the original radon in the water has decayed away and the radon measured than is ^{222}Rn in equilibrium with ^{226}Ra dissolved in the water sample. This second measurement allows for the easy determination of radium concentration in water.

3. Experimental Results

3.1. PSA optimization

The new liquid scintillation counters have the ability to discriminate between alpha and beta particles by pulse-shape discrimination (PSD) based on pulse-shape analysis (PSA). The discrimination of alpha and beta pulses is based on the well-known difference between the delay component of their decay.[18] Typically, alpha-produced events have longer decay lifetimes than beta events. This is due to the fact that it takes a longer time for the cocktail to release its excitation energy as light when the excitation is caused by an alpha particle in comparison with a beta particle. However, with alpha and beta emitters simultaneously present in the sample there is no absolute separation of the counts. Some counts due to alpha particles my be recorded in the beta counting window and vice-versa, originating a partial cross over.

In order to select the PSD parameter best value, the optimization of pulse-shape analysis was made measuring separately an α emitter (^{241}Am) and a β emitter (^{36}Cl). ^{241}Am is an alpha emitter (E_α = 5.54 MeV) with a weak emission of gama rays (E_γ = 59 keV). ^{36}Cl is a pure beta emitter ($E_{\beta max}$ = 709.55 keV) with no alpha particle emission. After counting the pure alpha emitter source, the percent of alpha events that were counted as beta events is plotted on the discriminator setting. Similarly, the events recorded as alpha emissions in the counting of the pure beta emitter source were plotted also in same graph in percent of total counts, against the discriminator setting. Figure 1 shows the spillover curve obtained with ^{241}Am and ^{36}Cl standards.

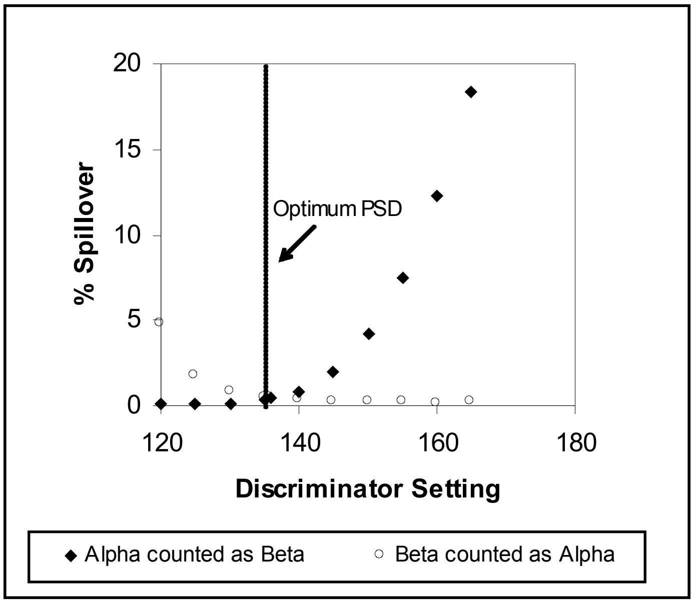

Figure 1 - Cross over plot using ^{241}Am and ^{36}Cl standard sources

The pulse decay discriminator setting chart (% spillover vs time) was a typical α/ β crossover plot for ^{241}Am/ ^{36}Cl radionuclides.[19] The optimum PSD level was obtained setting the discriminator at 136. For this PSD value the percent spillover for alpha and beta events is kept at a minimum, 0.41% and 0.40% for alpha and beta particles, respectively. Using this PSD value the counting efficiency for each standard source was 98.25% and 99.74 % for the ^{36}Cl and ^{241}Am, respectively. This discriminator setting was used later in the counting of alpha/beta activities in real water samples.

3.2. Method validation for gross alpha/beta measurements

To validate the method were needed pure alpha and beta reference sources matching the chemical and physical characteristics of environmental samples to be measured. For this purpose, in a first stage, pure alpha (^{241}Am) and pure beta (^{90}Sr/ ^{90}Y) reference sources were prepared with activities ranging from 1 to 25 Bq l^{-1}. With this sources, the efficiency for alpha and beta emitters was determined at 97.1 % for ^{241}Am standards and 91.4 % for ^{90}Sr/ ^{90}Y, with PSD set at 136 (Tables 1 and 2).

Table 1 - Counting efficiency at different ^{241}Am concentrations

^{241}Am standard activity (Bq l^{-1})	Counting efficiency (%)
24.25	101.72 ± 0.35
12.13	98.79 ± 0.47
4.85	98.28 ± 0.75
1.21	89.53 ± 1.41

Average ± 1 S.D. = 97.08 ± 0.42 Bq l^{-1}

Table 2 - Counting efficiency at different ^{90}Sr concentrations

^{90}Sr standard activity (Bq l^{-1})	Counting efficiency (%)
23.90	91.74 ± 0.23
11.95	92.75 ± 0.32
5.97	91.29 ± 0.45
1.19	91.04 ± 0.98

Average ± 1 S.D. = 91.70 ± 0.38 Bq l^{-1}

In a second stage, in order to validate the proposed method for determination of gross alpha/gross beta measurements, tap water samples spiked with ^{241}Am and ^{90}Sr were prepared. Tap water samples without added radioactivity were used as background. The counting time for the background and the samples was 240 minutes and the pulse shape discriminator was set at PSA = 136. The nominal activities of spiked samples and results obtained by measurements are shown in Table 3. There is an excellent agreement between both values.

Table 3 - Alpha and beta measurements for water samples spiked with known activity of ^{241}Am and ^{90}Sr

Alpha Activity (^{241}Am, Bq l^{-1})	
Known$^{(a)}$	Measured$^{(b)}$
48.5	45.98 ± 1.70
24.25	23.47 ± 1.56

11.64	10.90 ± 1.48
5.82	5.65 ± 0.05
1.16	1.03 ± 0.06
Beta Activity (^{90}Sr, Bq l^{-1})	
Known(a)	Measured(b)
23.90	24.76 ± 0.05
11.95	12.38 ± 0.12
5.17	5.35 ± 0.02
1.19	1.21 ± 0.01

(a) Uncertainty of the nominal value of activity is 0.47 % and 0.88% for ^{241}Am and ^{90}Sr, respectively.

(b) Average of the measurement of three replicate samples with the same nominal activity.

3.3. Calibration tests for ^{222}Rn and ^{226}Ra measurements

In order to determine the counting efficiency for ^{222}Rn and ^{226}Ra measurements and to check the linear response of the counter to different ^{226}Ra concentrations, a set of ^{226}Ra standards were prepared with Opti-Fluor-O (Packard) cocktail as described in section 2. This cocktail, based on high flash-point solvent Linear Alkylbenzene, was chosen to obtain two immiscible phases when we add the water sample to the organic cocktail in the scintillation vial. With this cocktail ^{226}Ra is not extracted into the organic phase, remaining dissolved in the aqueous phase, and does not contribute to the counts recorded. The activity measured is due to ^{222}Rn only, which diffuses into the organic phase. Thirty eight days after closing the vial ^{222}Rn is in equilibrium with

^{226}Ra. For the counting a wide open window was applied in order to integrate the contributions of all alpha and beta particles emitted in the decay chain of ^{222}Rn through to ^{214}Po. At equilibrium, for every radon α-decay there are three alpha particles (from ^{222}Rn, ^{218}Po and ^{214}Po) and two beta particles (from ^{214}Pb and ^{214}Bi) emitted in a rapid sequence of nuclear desintegrations. Each individual particle is counted with an efficiency close to 100 %.[20] In the case of our ^{226}Ra sources, the counting efficiency for ^{226}Ra in equilibrium with the daughters was 481.86 % due to the cumulative contribution of the radioactive emitters by the short-lived progeny of radon (Table 4). Similar values were reported by other authors.[21]

Table 4 - Counting efficiency for ^{226}Ra standards

^{226}Ra standard activity (Bq l^{-1})	Counting efficiency (%)
22.13	477.03 ± 2.41
11.10	472.28 ±. 3.38
4.44	490.09 ± 5.39
1.11	500.23 ± 10.58
0.44	469.70 ± 15.48

Average ± 1 S.D. = 481.86 ± 5.78 $Bq.l^{-1}$

Figure 2 shows the linear response of the counter to different ^{226}Ra concentrations, measured in the conditions of a closed system in radioactive equilibrium between ^{226}Ra and ^{226}Ra decay products. This linear response demonstrates also that no ^{222}Rn leaks occurred from vials during the storage time.

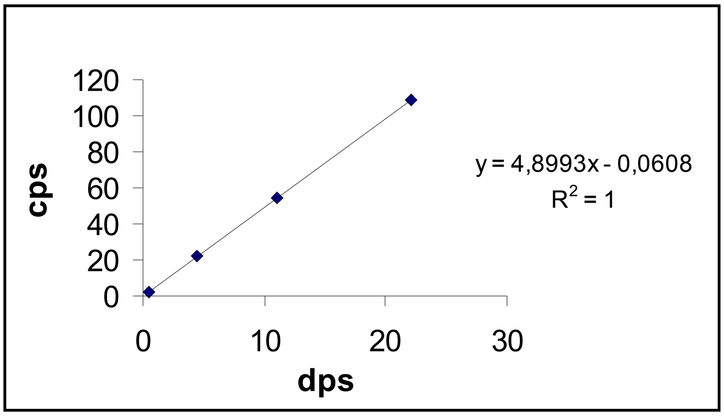

Figure 2 - Plot of cps (counts per second) vs dps (desintegrations per second) for a set of ^{226}Ra standard solutions

To follow the ingrowth of ^{222}Rn with time until the formation of radioactive equilibrium, two set of three replicates ^{226}Ra standard solutions with 31 Bq l^{-1} and 15.5 Bq l^{-1} respectively, were measured for up to nearly 40 days following the preparation of the samples. Thirty days after sealing the vials and thereafter, the counts recorded become nearly constant. At this point ^{222} Rn is in near radioactive equilibrium with ^{226}Ra (Figure 3). Using this method, water samples with unknown concentrations of ^{226}Ra can be measured and the ^{226}Ra concentration present in water can easily be determined using the efficiencies reported above.

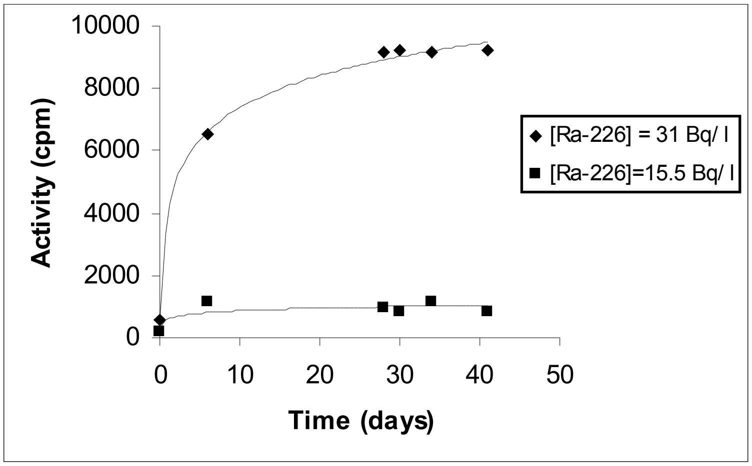

Figure 3 - Temporal evolution of the average activity of two different ^{226}Ra solutions

Figure 4 shows the decay of ^{222}Rn activity in three natural water samples measured shortly after collection and containing ^{222}Rn in excess compared with ^{226}Ra activity. After 30 days no more ^{222}Rn in excess is present in the samples. The radon activity remains constant and it is supported by the decay of ^{226}Ra present in the aqueous phase. The computed half-time for the decay observed during the inicial 15 days is near 4 days confirming that the decrease of the activity is due to radon decay only ($T_{1/2}$ = 3.8 d).

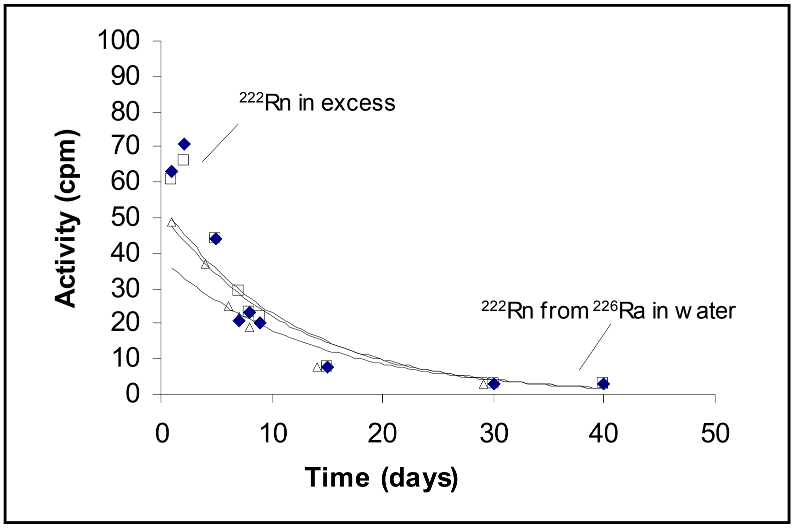

Figure 4 - Activity of ^{222}Rn in natural water samples with time

Analysis of the spectra obtained using this two phase sample vials, corroborates that in the spectrum only ^{222}Rn and its short lived progeny contribute to the counts. A typical pulse-height spectrum for radon and its daughters is shown in Figure 5.

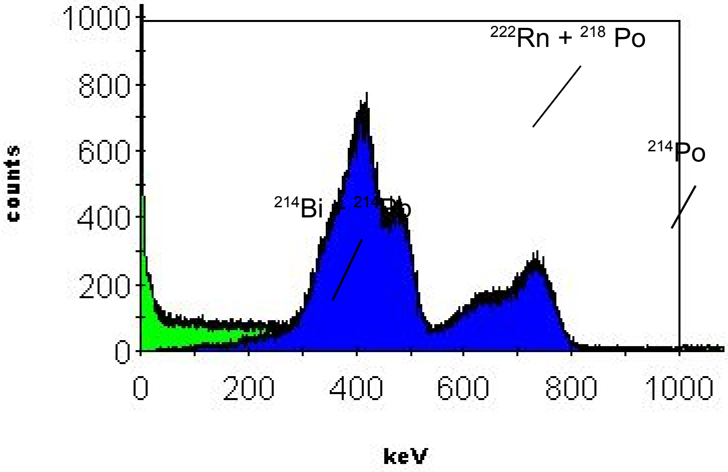

Figure 5 - A pulse-height spectrum obtained for a ^{226}Ra standard (22.3 Bq) recorded 30 days after capping the liquid scintillation vial.

4. Application of the LSC Technique to Environmental Samples

After the method validation described in section 3, the LSC technique was applied in radioactivity measurements of drinking water and surface waters. Results for gross alpha and gross beta activities are presented in Table 5.

Gross beta activities range from the low level detection limit value (LLD) 0.052 Bq l^{-1} to 6.54 Bq l^{-1} and the values of gross alpha measurements from 0.022 Bq l^{-1} (LLD) to 7.27 Bq l^{-1}. The values are within the limits approved by law for radioactivity in water for human consumption with the exception of sample number 5. However, this sample is a mineral water which is not covered in the EU recommendation.

Table 5 - Gross alpha and beta measurements in drinking waters

Number of sample	Type of water	Gross beta (Bq l^{-1})	Gross alpha (Bq l^{-1})
1	Tap	0.190 ± 0.034	<0.022
2	Tap	0.127 ± 0.044	0.120 ± 0.017
3	Tap	0.101 ± 0.051	<0.022
4	Tap	<0.052	<0.022
5	Bottled mineral	6.54 ± 0.105	7.27 ± 0.084
6	Bottled	<0.052	<0.022
7	Bottled	0.224 ± 0.041	0.107± 0.018
8	Tap	0.100 ± 0.036	<0.022
9	Tap	0.189 ± 0.034	<0.022

10	Tap	0.269 ± 0.033	<0.022
11	Tap	0.179± 0.033	<0.022
12	Tap	0.162 ± 0.030	<0.022

The LSC technique has been used for radon measurements in drinking water samples from municipal supplies, drinking water from local supplies in small villages and non drinking water from ponds, including artificial ponds and in old open-pits mines in the granite rock. Values presented in Table 6 illustrate the concentration levels found in the centre and north regions of the country. Radon measurements range from the low level detection limit (LLD) 0.195 Bq l^{-1} to 349.15 Bq l^{-1}.

Table 6 - Radon measurements in water from municipal supplies and open ponds

Site	Type of water source	Radon activity (Bq l^{-1})
Guarda	Tap(a)	35.24 ± 1.60
Lamegal	Tap(a)	48.58 ± 2.03
Vila Fernando	Tap(b)	349.15 ± 6.39
Freixeda	Tap(b)	166.52 ± 4.30
Sobral da Serra	Tap(a)	<0.195
Mondego Sul	Pond(c)	34.89 ± 1.88
Ázere	Tap(a)	<0.195
Fontinha	Pond(c)	14.02 ± 0.95
V. N. Tázem	Tap(a)	1.90 ± 0.19
Maria Dónis	Pond(c)	24.28 ± 1.27

Trancoso	Tap(a)	112.77 ± 3.23
Aguiar da Beira	Tap(a)	61.29 ± 2.29
Corga do Valbom	Pond(c)	33.01 ± 1.55
Esmolfe	Tap(b)	198.09 ± 4.41

(a) Tap water from the municipal distribution supply system.
(b) Drinking water from the village local water supply (spring source or aquifer)
(c) Pond either natural or in an old open pit of a former uranium mine.

5 - Conclusions

The use of a low background liquid scintillation counting system with pulse shape analysis enables the simultaneous determination of alpha and beta activities in water samples with counting efficiencies up to near 100% both for alpha and for beta particles. The LSC technique is a good alternative to the conventional radiochemical method used for monitoring gross alpha and beta activities, based on counting a thin layer source containing the salts residue. Measurement of spiked water samples showed that the LSC method is suitable for the determination of gross alpha and beta activities in drinking water routine monitoring, using counting times of 240 minutes. Detection limits are 0.022 Bq l^{-1} and 0.052 Bq l^{-1} respectively for gross alpha and gross beta, at 95% confidence level. The LSC method is also very convenient for ^{222}Rn and ^{226}Ra measurements in drinking water samples. This method requires minimal sample pretreatment and its low detection limit makes it ideal for environmental monitoring of radioactivity in water. A lower limit of 0.195 Bq l^{-1}using counting times of 60 minutes, is sufficient for control purposes of radiological quality of water for human consumption. Furthermore, this technique has been also successfully applied to monitor radioactivity, including dissolved radon, in mine waters from old uranium mines.

References

[1] Diário da República, Decreto-Lei nº 243/2001 of September de 2001.

[2] European Commission Recommendation 344/ 85 of 20 December de 2001.

[3] Sequeira. M. M; Faísca, M. C.; Ferrador, G.; Reis, M.; Curado, S.; Pires, C.; Silvino, V. Pereira; Tavares, M. A.; Gameiro, M. A.; Madruga, M. J. “Vigilância Radiológica a Nível Nacional”, Relatório DPRSN, Série A, nº18/ **2002**.

[4] Carvalho, F. P.; Madruga, M. J.; Ferrador, F.; Lopes, I; Sequeira, M.; Silvino, V. “Controlo da Radioactividade na água para o abastecimento público” Relatório DPRSN, Série A, nº22/ **2002** (Simpósio Luso-Brasileiro de Engenharia Sanitária e Ambiental, Braga, Setembro 2002).

[5] Madruga, M. J.; Carvalho, F. P. ; Sequeira. M. M; Ferrador, G.; Reis, M.; Gameiro, M. A.; Gouveia, J.; Ramos, L.; Oliveira, J. M.; Silvino, V.; Machado, L.; Faria, I.; Lucas, A.; Pereira, M. A.; Tavares, M. A.; Libânio, A.; Pires, C., Curado, S. Relatório DPRSN, Série A, nº26/ **2003**.

[6] - NP 4332 (1996) Measurement of gross alpha activity in non saline water. Thick source method. Portuguese Law, IPQ, **1997**.

[7] - NP 4330 (1996) Measurement of gross beta activity in non saline water. Thick source method. Portuguese Law, IPQ, **1996**.

[8] Sanchez-Cabeza, J. A.; Pujol, Ll. "A Rapid Method for the Simultaneous Determination of Gross Alpha And Beta Activities in Water Samples Using a Low Background Liquid Scintillation Counter", *Health Phys.*, **1995**, 68, 674-682.

[9] Sanchez-Cabeza, J. A.; Pujol, Ll.; Merino, J.; León L.; Molero, J.; Vidal-Quadras, A.; Schell, W. R.; Mitchell, P. I. " Optimization and Calibration of a Low-Background

Liquid Scintillation Counter for the Simultaneous Determination of Alpha and Beta Emitters in Aqueous Samples", *Radiocarbon*, **1993**, 43-50.

[10] Prichard, H. M., Gessell, T. F., “Rapid Measurments of ^{222}Rn concentrations in water with a Commercial Liquid Scintillation Counter” *Health Phys*. **1977**, *33*, 577.

[11] Schönhofer, F.; Barnet, J. M.; Mcklveen, J. M. "Determination of^{222}Rn e ^{226}Ra in drinking water by low-level liquid scintillation counting-surveys in Austria and Arizona" in Liquid Scintillation counting and Organic Scintillators, by Ross, H.; Noakes, J. E.; Spaulding, J. D. Lewis Publishers, inc. **1991**, 48, 537-545.

[12] Chereji, I. "^{222}Rn (^{226}Ra) Determination in water by scintillation methods" *J. Radioanal. Nucl. Chem. Letters,* **1992**, 165, 263-267.

[13] Burnett, J. M.; Holbert, K E.; Stewart, B. D.; Hood, W. K. "Lung dose estimates from ^{222}Rn in Arizona groundwater based on liquid scintillation measurements" *Health Physics,* **1995**, 68, 699-703.

[14] - Burnett, W. C.; Christoff, J.; Stewart, B.; Winters, T.; Wilbur, P. "Reliable Gross Alpha-/ Beta- Particle analysis of Environmental samples via liquid Scintillation Counting", *Radioact. and Radiochem.,* **1999**, 11, 26-44.

[15] "Introduction to sample Preparation for Alpha/ Beta LSC", Packard Company, **1993**.

[16] Vitz, Ed “Toward a standard Method for Determining waterborne Radon” *Health Phys.*, **1991**, 60, 817-829.

[17] Kitto. M. E. “Characteristics of liquid scintillation analysis of radon in water” " *J. Radioanal. Nucl. Chem.* **1994**, 185, 91-99..

[18] Knoll, G. F. "Radiation Detection and Measurement", New York, John Wiley & Sons, **1989**, 752.

[19] Spaulding, J. D.; Noakes, J. E. " Determination of ^{222}Rn in Drinking Water using an Alpha/Beta Liquid Scintillation Counter" Liquid Scintillation Spectrometry 1992, by Noakes, J. E.; Schönhofer, F.; Polach, H. A., *Radiocarbon*, **1993**, 373-381.

[20] Parsa, B.; Horton, T. "Radon-222 in drinking water " *Health Phys.*, **1990**, *58*, 209

[21] Salonen, L. "Measurement of low levels of ^{222}Rn in water with different comercial liquid scintillation counters and pulse - shape analysis" in Liquid Scintillation Spectrometry 1992 by Noakes, J. E., Schönhofer, F. Polach, H. A. Radiocarbon **1993**, 361-372.

EXAMINING THE NATURALRADIOACTIVITY OF WATER SOURCES TO EVALUATE THE IMPACT ON SURROUNDING COMMUNITIES

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Abstract

Natural occurring radioactive materials (NORM) are quite common in the South African mining and mineral processing industry, even so that uranium is produced as a by-product at certain gold and copper mining sites. Other major industries associated with NORMs are the coal, copper and heavy mineral sectors.

Legislation in South Africa addresses the allowed yearly radiation dose to registered radiation workers and the general public, and adheres to the most common internationally accepted standards of 20 mSv/a and 1 mSv/a respectively for these categories. The yearly dose is obviously the sum of the contributions from every

individual nuclide from all possible sources. Accordingly, for members of the public, the individual sources are to be evaluated at the (South African) guideline level of 25 μSv/a. This imposes severe constraints on the radioanalytical laboratory to offer an affordable routine service due to the required sensitivity to analyse these NORMs and the variety of matrices involved.

Determination of all required parameters to evaluate the yearly dose is possible, although costly. Correlations of yearly dose with one or two chemical/radionuclide components will allow an affordable monitoring strategy. According to the evaluation of a survey performed in one of the gold-mining catchment areas in South Africa this seems indeed possible.

1 Introduction

In the Republic of South Africa artificial radioactivity is associated with the generation of nuclear power and operation of smaller research facilities. They have only a power plant situated at Koeberg and an accelerator facility in Faure, both near Cape Town in the south, and a small nuclear research reactor at the Atomic Energy Corporation (AEC), Pelindaba, near Pretoria in the north. The AEC formerly enriched its own uranium and manufactured fuel elements both for the Koeberg and Pelindaba sites. The research reactor is mainly used for production of medical and industrial isotopes, silicon irradiation, colour modification of gemstones, neutron diffraction for industrial applications and neutron activation analysis.

Natural radioactivity goes with the vast mineral resources in such concentrations that the nuclides from the natural uranium, thorium and actinium decay series are found to pose concern for occupational exposure at certain mining and mineral processing industries, and public exposure to communities living around these areas. The main industries concerned are the gold, copper, heavy mineral sand and the coal mining and processing operations.

The radiological impact of all operations is monitored as part of the license obligations, imposed by the South African Nuclear Energy Act (1). The Council for Nuclear Safety is mainly concerned about the impact on workers and the release of effluents and dust to the environment, while the Department of Water Affairs & Forestry is intensively studying the concentration of radionuclides in identified catchment areas around the mining and mineral processing sites to assess the impact on the public using these water sources as part of their dietary intake.

The occupational exposure at the Koeberg Nuclear Power Station (2) showed an average value of about 0,90 mSv for the years 1994 and 1995. Liquid and gaseous effluents discharged from this plant in 1995 resulted in a calculated radiation dose to the public of about 0,45 mSv per year. Data for the operation of the AEC (2) site showed an average occupational exposure of 0,59 mSv for the year 1995, while the public exposure due to airborne effluent discharges was calculated at a maximum of 12 μSv per year for 1995.

Compared with the nuclear industry, the occupational and public exposure imposed by the mining and mineral processing industries is more difficult to assess due to the numerous potential transport mechanisms and pathways of the natural radioactivity. Preliminary data show that occupational exposure due to inhalation of respirable dust could be substantial if no proper preventions are made. Yearly doses could be as high as 40 mSv per year in certain areas of the uranium, copper and heavy mineral processing industries. Recent monitoring of surface and borehole water in catchment areas around the major gold mining activities revealed that public exposure could accumulate up to 0,5 mSv per year, if these water source were the main sources of drinking water available to the communities living in and around this area.

Assessment of the yearly dose from the natural radionuclides of the uranium, thorium and actinium series poses a major challenge to the Radioanalytical Laboratories of the Atomic Energy Corporation of South Africa. At large about 25 individual nuclides are to be assessed which all have their own individual dose conversion factors (3). In practice, after assuming radioactivity equilibrium between short-lived daughters with their respective parents, one has to determine about 12 long-lived nuclides. The concentration levels to be analysed for, however, differ vastly from nuclide to nuclide, and also depend on the yearly intake through ingestion and/or inhalation. The first order dose assessment is based on certain default intake values (4), and a dose screening level of 25 μSv per year per individual source (4).

Some of the NORMs, specifically ^{238}U, ^{235}U and ^{232}Th, can be determined conveniently with instrumental neutron activation analysis or ICP-MS. However, the majority requires (radio)chemical separation procedures followed by mass spectrometry or radiation detection. The original matrix may vary between drinking water, foodstuffs and respirable airborne dust which all require an individual approach to analyse their natural radionuclides. For drinking water one should be able to analyse nuclides like ^{227}Ac, ^{231}Pa, ^{228}Ra, ^{210}Po, ^{210}Pb and ^{232}Th at typically a lower limit of determination (LLD) of about 1 mBq/L. For certain foodstuffs one is faced with an LLD of around 1 mBq/kg, which poses again problems with dissolution to allow radiochemical separations as direct measurements by γ-ray spectrometry are not adequately sensitive for all nuclides of interest to assess the yearly dose. With respirable airborne dust one faces the problem of limited sample quantities. This requires a specific analysis protocol, which again places severe constraints on the turnaround time of the analyses. All these factors, together with the economic requirement to produce large quantities of data at low costs challenges the capabilities of our Radioanalytical laboratories (at present 31 staff members).

2 The Radioanalytical Infrastructure

Most national and commercial nuclear centres throughout the world have access to a variety of nuclear and related analytical techniques. The basic requirements for analysis of NORMs at high sensitivity are instrumental neutron activation analysis (INAA), inductively coupled plasma mass spectrometry (ICP-MS), high- and low-energy γ-ray spectrometry (HEGS & LEGS), α-particle spectrometry (APS), liquid scintillation counting (LSC) and radiochemical separation techniques for the elements Po, Pb, Ra, Ac, Pa, Th and U. In addition to these the laboratory should cater for sample conservation, representative sub-sample preparation and sample dissolution/destruction. An adequate QA/QC system is mandatory. This last aspect is vital to avoid disputes between possible polluters and the national regulatory authorities on the reliability of the data produced.

3 The Matrices Involved

The major pathways of NORM intake by the public are via inhalation of respirable airborne dust and ingestion of foods and liquids. The yearly intake of NORMs via inhalation depends on the respiration rate(5), which is age and profession related, the concentration of the airborne dust and the concentration of the individual nuclides in the respirable fraction of the dust. This aspect is important as large differences in nuclide concentrations have been observed as a function of particle size. Intake via ingestion depends on the dietary habits of the affected groups and/or individuals (which are also age related), and the concentration of the radionuclides concerned. To allow a first order assessment of the radiological impact, default values for consumption may be assumed. Typical values for the South African environment(4) are shown in Tables 1 and 2. Other aspects to be dealt with are the fresh/dry ratio and specific mass of the dried food matrices. The variable volatility of the elements concerned, and even isotopes of the same element, prevent preconcentration by ashing at elevated temperatures. The specific mass of dried products allows estimating the sensitivity of instrumental techniques like γ-ray spectrometry. Some typical values observed in our laboratories are provided in Table 3.

4 The Dose Conversion Factors

Dose conversion factors (DCF) can be obtained from literature(3). The applicable data for the nuclides from the natural uranium, actinium and thorium decay series are presented in Tables 4 to 6 for exposure of the general public and (registered radiation) workers due to ingestion and inhalation respectively. It should be emphasised that the DCF's are age related and dependent on particle size.

5 A Case Study: Evaluation of the Mooi River Catchment

5.1 Introduction

During 1997 the Department of Water Affairs and Forestry (DWAF) performed a survey of one of the major catchment areas influenced by the gold mining industry on the West Rand. During the first phase of the study some 1000 samples collected from about 40 monitoring points were collected and analyzed for their gross α/β-activity, uranium, thorium and radium content. During the second phase some 100 samples were collected at about twenty monitoring sites and analyzed for a comprehensive suite of NORMs. The average dose for the individual monitoring points has been calculated from the natural radionuclide data, the age dependent dose conversion factors (3) and the default consumption rates (4). To obtain a first order estimation of the yearly dose throughout the catchment area an age-group weighed average lifetime dose was calculated assuming a life span of 70 years, although the most critical groups are the age group of <1 year old followed by the age group between 12 and 17 years old. The radionuclide data showed a dominance of the uranium activity, and accordingly the correlation between the yearly dose and the uranium concentration has been evaluated. This would provide a practical solution to monitor this specific catchment, although care should be taken to use the correlation's obtained for all catchments in South Africa. The impact on the various age groups has been evaluated and it is anticipated that application of the lifetime average dose would provide a fair tool to establish the yearly dose received by potentially affected communities and/or individuals.

5.2 Data Base

Due to budgetary constraints not all nuclides of the natural uranium, thorium and actinium decay series were determined. The first phase provided data for U-238, U-235, Th-232, Ra-226, Ra-224 and Ra-223, while sampling was performed weekly during the first 6 months of 1997. The second phase of the study, during the second semester of 1997, provided results for most of the longer lived nuclides (U-238, U-235, U-234, Th-232, Th-230, Th-228, Th-227, Ra-228, Ra-226, Ra-224, Ra-223, Pb-210 and Po-210) on eighteen of the original forty-one monitoring points. Pa-231 and Ac-227 were only measured on three of these eighteen sampling sites showing elevated uranium concentrations.

5.3 Quality Assurance

Additional to an intercomparison study on uranium, thorium and radium analysis between two national and one overseas laboratory the quality assurance program included the application of independent radiochemical and ICP-MS techniques for the determination of U-238, U-235 and Th-232 in the second phase of the survey. The correlation between the two techniques could be evaluated from the obtained U-238 and U-235 data (Th-232 was frequently detected at the lower limit of determination by ICP-MS and accordingly not reliable for correlation evaluations). The following correlation ([U] in µg/L) was obtained for the 98 samples surveyed in the second phase of the study (see Graph D):

[U] (ICP-MS) = 0,993 x [U] (Radiochemical) - 0,563 $R^2 = 0{,}906$

In natural uranium the activity ratio between U-238 and U-235 is 21,719. The following relations were obtained from linear regression between the relevant data obtained both by radioanalytical and ICP-MS analyses:

Radioanalytical (Second phase; 98 data): U-238/235 ratio = 21,341 ± 0,115 $R^2 = 0{,}996$

ICP-MS (Second phase; 63 data): U-238/235 ratio = 22,171 ± 0,571 $R^2 = 0{,}860$

ICP-MS (First phase; 570 data): U-238/235 ratio = 20,785 ± 0,030 $R^2 = 0{,}999$

Accordingly it can be concluded that both set of data as well as the radiochemical determination of all other nuclides can be accepted to provide a fair representation of the nuclide composition of the sites surveyed in the whole 1997 study of the Mooi River catchment.

5.4 Assumptions in Dose calculations

To enable an “all nuclide” dose calculation the following had been assumed for the radioactivity of the various nuclides of the NORM series. These assumptions are made on the respective half-lives of all members of the decay series and the individual nuclides measured during the survey:

- \- Th-234 and Pa-234m to be in equilibrium with U-238,
- \- Rn-222, Po-218, Pb-214, Bi-214 and Po-214 to be in equilibrium with Ra-226,
- \- Bi-210 to be in equilibrium with Pb-210,
- Th-231 to be in equilibrium with U-235,
- Rn-219, Po-215, Pb-211, Bi-211 and Tl-207 are in equilibrium with Ra-223,
- \- Ac-228 to be in equilibrium with Ra-228, and
- \- Rn-220, Po-216, Pb-212, Bi-212, Po-212 and Tl-208 in equilibrium with Ra-224.

Ac-227 at the time of sampling was calculated from two consecutive determinations of Th-227. The results for the three monitoring points surveyed for actinium (18 data) showed a good correlation between these mother-daughter nuclides (with a Th/Ac ratio of 6.12 ± 1.69). Accordingly the activity for the remainder of the samples in the second phase of the survey was estimated from the Th-227 data obtained.

Pa-231 did not show any direct correlation between the sampling points surveyed for this nuclide and the average concentration observed (0.2 ± 0.9 mBq/L) was taken as the default value for the global mean of the second phase of the Mooi River survey.

5.5 Dose Calculations and Correlations

According to the outline in 5.4 the evaluation has been performed for the most critical groups (i.e. the < 1 year olds followed by the age group between 12 and 17 years old) and the calculated lifetime average exposure. The calculations were done to allow proper evaluation of the dose received during the one year period and to evaluate the possibility of using one unique monitor for the Mooi River catchment to estimate the yearly dose (instead of doing a full nuclide specific analysis). From the two sets of data (i.e. the "all nuclide" dose for the first and the second semester of 1997 for the eighteen corresponding sites; with the omission of one point that dried up during the second phase) the average "all nuclide" dose was calculated. The results are shown in Table A for the lifetime average evaluation, the age group between 12 and 17 year old and the age groups of < 1 year old respectively.

From the phase 1 and phase 2 data the average uranium concentration was calculated. The linear regression between the average uranium concentration and the average "all nuclide" dose was calculated, using all monitoring sites in the evaluation. The following correlations were obtained, the last correlation being graphically represented in Graph A.

< 1 year old: [All nuclide dose] (mSv/a) = 0,00409 x [U] (µg/L) + 0,063 (R^2 = 0,932)

12 - 17 year old: [All nuclide dose] (mSv/a) = 0,00275 x [U] (µg/L) + 0,020 (R^2 = 0,901)

Lifetime average: [All nuclide dose] (mSv/a) = 0,00124 x [U] (µg/L) + 0,017 ($R^2 = 0,970$)

The good correlation obtained between uranium and dose is due to the higher solubility of uranium compared to the other nuclides of the natural decay series. Additional to this it is observed that a good correlation exists between U-238 and Ra-226 and Ra-226 and Ra-223, with other nuclides at either very low concentrations or relatively constant over the entire catchment (Pb-210). Some correlations are graphically shown in Graph B1-14.

5.6 Estimation of the Possible Uncertainties

Possible uncertainties in the estimation of the yearly dose received from drinking environmental (untreated) water in the Mooi River catchment will arise from analytical uncertainties, environmental variations, the applied uranium to dose correlation curve, the age dependant default intake values and the sampling frequency.

a The analytical uncertainty can be estimated from the uranium results obtained in the second phase study by both the radiochemical and ICP-MS analysis techniques. The correlations between the uranium concentration and the “all nuclide” dose described in paragraph 5.5 have been determined using the radiochemical uranium database. The same evaluation based on the ICP-MS uranium data showed the following correlations:

< 1 year old: [All nuclide dose] (mSv/a) = 0,00415 x [U] (µg/L) + 0,065 (R^2 = 0,922)

12 - 17 year old: [All nuclide dose] (mSv/a) = 0,00273 x [U] (µg/L) + 0,024 (R^2 = 0,889)

Lifetime average: [All nuclide dose] (mSv/a) = 0,00124 x [U] (µg/L) + 0,017 ($R^2 = 0,964$)

These data compare well with the correlation observed from the radiochemical uranium determination. The difference in the calculated dose based on radiochemical and ICP-MS analysis at a dose level of 75 µSv/a is about 2%, 4% and 1,5% for the respective age groups of < 1 year old, between 12 and 17 years old and the lifetime average evaluation. Table B provides the summed data on the linear regression and dose calculations.

b Environmental variations can be estimated from the standard deviation observed for the individual nuclide analyses in phase 1 and phase 2 of the study. Again the total yearly dose correlation has been calculated, now using the "upper" and "lower" bound regions of the analytical data (i.e. the average concentrations plus and minus one standard deviation respectively). The correlations were determined using both the Radiochemical and ICP-MS uranium data sets obtained in phase 2 of the study. Once more, both sets did not show substantial differences and accordingly the mean values were taken to evaluate the yearly fluctuation in the dose. The data for the critical groups (i.e. the < 1 year old followed by the age group between 12 and 17 years old) and the lifetime averages are shown in Table C. From this it may be observed that at around an estimated average yearly dose of 100 µSv/a the "upper" limits of the evaluated dose will not vary more than about 20%, 30% and 50% for the respective lifetime average evaluation and the age groups 12 to 17 years old and < 1 year old. This shows that the calculated yearly dose based on average yearly nuclide concentrations will provide a fair estimation of the radiological impact on the public.

c The applied uranium to dose correlation curve will show a slight variation if sampling sites would be randomly omitted from the regression calculations. This uncertainty will be less than 10% due to the high degree of correlation between the measured uranium concentration and the estimated yearly dose. Omission of sampling site 12 which dried-up during the second phase of the survey, showing high nuclide concentrations during the first phase, will cause a difference of plus 6% in the calculated dose levels around 100 µSv/a, while the omission of the sampling site showing the highest average uranium concentration during the monitoring period will give a 3% negative deviation at about 100 µSv/a (see Table D).

The expected uncertainty in the obtained correlation between the yearly dose and the uranium concentration for the Mooi River catchment will be less than 10%, provided statistically reliable average uranium data are obtained (e.g. through monthly monitoring).

d The age dependent default intake values are prone to a large uncertainty in the yearly dose evaluation. It should be emphasized that default intake rates are used in the dose calculations, i.e. assuming daily intake from the same source and assuming that the source is the only available source to the individuals concerned. Accordingly, at sites showing potentially elevated dose levels (e.g. above 100 µSv/a) due to default water intake one should determine the actual yearly consumption from the source by the communities and/or individuals concerned.

e The influence of the sampling frequency on the calculated yearly dose can be estimated best from the uranium data obtained in phase 1 on the Mooi River catchment study. The average concentrations were calculated for the individual sites together with the four-weekly average, shifting the intervals by one week respectively. One would thus obtain the average concentrations for uranium at the following four intervals:

Weeks 1, 5, 9, 13, 17, 21 Weeks 2, 6, 10, 14, 18, 22
Weeks 3, 7, 11, 15, 19, 23 Weeks 4, 8, 12, 16, 20, 24

Comparison of the minimum and maximum difference between these individual data and the average concentration observed over the entire sampling period provides an estimate of the possible over- or underestimation of the uranium concentration. In this model the sites not sampled at a particular date were regarded as not being accessible, although for dose calculations one should “dry” sites regard as having zero uranium concentration as they are not contributing to the yearly dose at that specific time.

Table E shows the compiled data for phase 1 and the observed uranium ratio between phase 1 and phase 2. The following observations are made:

- Four-weekly sampling compared to weekly sampling can over- or underestimate the yearly dose by a factor of up to 3. (Site 38 being discarded due to infrequent sampling).
- The data obtained in the second phase can not clearly be related to seasonal influences. Sampling sites 35 and 36 show increased levels of uranium during the second semester not readily explained by sampling frequency variations. Sampling site 12 showed a decreased uranium content in the second phase of the study; this site dried up due to decreased/ceased input of waste water directly related to the gold mining activities.

5.7 Suspended Solids

The suspended solids from the 15 sites sampled in the last batch (December 1997) of the Mooi River survey have been analyzed semi-quantitative for their α-active natural nuclides. The yearly dose was calculated for both the suspended solids and the residual water fractions. Evaluation showed the following influence of the suspended solids on the yearly dose relative to the contribution from the residual water fraction:

Age group	**Average**	**Median**	**Maximum**	**Minimum**
< 1 year old:	(1,3 ± 1,2)%	1,2%	5,0%	0,0%
12 - 17 years old:	(2,5 ± 2,4)%	2,0%	8,3%	0,1%
Lifetime average:	(2,3 ± 2,1)%	1,9%	7,6%	0,1%

Contributions to the dose from the suspended solids came mainly from the radionuclides ^{210}Pb/^{210}Po, ^{227}Ac, ^{230}Th, ^{231}Pa and ^{232}Th, while ^{238}U/^{234}U and ^{226}Ra governed the residual water. This clearly indicates the distinction between the solubility of the various radionuclides in the environmental eco-systems of the Mooi River catchment.

5.8 Measurement of Gross α/β-Activity

The use of gross α/β-activity data is restricted to primary screening surveys only. The data should not be used to assess non-identified radionuclides from limited nuclide specific information to estimate yearly doses. Evaluation of the data of phase 1 (922 data) showed that the gross α/β-activity, measured directly on the filtered water by liquid scintillation counting (LSC) on average agreed well with the calculated activities. The following linear regressions have been observed:

[LSC] Measured α-activity = 1,19 x Calculated α-activity $R^2 = 0{,}71$
[LSC} Measured β-activity = 1,01 x Calculated β-activity $R^2 = -\ 0{,}04$

This indicated that the gross α-activity measurement could be used as a screening tool, but that the β-activity measurements through direct LSC provide highly scattered data. In the second phase of the study the AEC took the initiative to evaluate the validity of the LSC data by applying an alternative technique through evaporation of the filtered water followed by gross α/β-activity measurement on a gas-flow counting system. The correlation through linear regression between the liquid scintillation (LSC) and evaporation (Evap) techniques (98 data) gave the following relations:

[LSC] α-activity = 0,82 x [Evap] α-activity + 0,10 $R^2 = 0{,}30$
[LSC] β-activity = 1,07 x [Evap] β-activity + 1,24 $R^2 = 0{,}20$

This indicated a fair correlation between the α/β-activities measured by both techniques, although the data are strongly scattered. Evaluation of the average gross activity data according to the same outline provided in paragraph 5.5 for the correlation between yearly dose and uranium concentration, gave the following results for lifetime average exposure:

[All nuclide dose] (mSv/a) = 0,02835 x [gross ∀] (Bq/L) + 0,021 R^2 = 0,856

[All nuclide dose] (mSv/a) = 0,02059 x [gross ∃] (Bq/L) + 0,017 R^2 = 0,779

Also here an environmental blank contribution of about 0,02 mSv/a is observed.

The contribution of radium

Physical observation of Graph A suggests a possible twin correlation between the measured uranium concentration and the estimated dose. Evaluation of the “upper” and “lower” correlation reveals that one can make a distinction between sampling sites correlated with mainly uranium contamination and those affected both by uranium and radium. Graph A2 provides the correlation curves with the following characteristics:

“Upper” correlation:

[All nuclide dose] (mSv/a) = 0,001431 x [U] (µg/L) + 0,01853 R^2 = 0,995

“Lower” correlation:

[All nuclide dose] (mSv/a) = 0,001025 x [U] (µg/L) + 0,01856 R^2 = 0,994

The upper correlation contained all “background” sites with uranium concentrations less than about 5 µg/L uranium (sites 6, 6a, 14, 18 to 20 and 24 to 36) together with high radium related sites (sites 10, 11, 12, 23, 15, 1, 2 and 39). The lower correlation contained all background sites together with sites that showed comparatively low radium concentrations (sites 7, 7a, 37, 38, 4, 9, 3, 5, 8, 13, 16, 17, 21 and 22). The nature of the increased/decreased mobility of radium at specific sites is not clearly understood yet. Future work is envisaged to find a correlation between the chemical constituents also measured during the survey and the observed radium mobility differences, although previous work performed by IWQS did not show any direct correlation between chemical constituents and radioactivity.

Furthermore a fair relation has been found between Ra-226 and Ac-227(Ra-223), as shown in Graph B9. This indicates that the mobility of actinium should not be underestimated due to its high degree of radiotoxicity.

5.9. The U-234 to U-238 Ratio

Literature (6) often indicates the U-234/238 ratio as a monitor to evaluate the origin of the source. A high ratio (> 2) and low concentration may indicate incongruent weathering from silicate rocks, while a low ratio (~ 1) and high concentration indicates congruent weathering from carbonate and sulfate sedimentary rock. Other studies (7) indicate that a low U-234/238 ratio in mining related areas suggest contamination of the water sources due to the mining and mineral processing activities. From the results obtained in the 1997 and 1998 surveys (see Graph E & E2 and Table F & F2) a possible indication can be found that a high concentration low ratio may indicate leaching from recently disturbed minerals, while a high concentration high ratio could indicate leaching from old tailings dams and dumps. This preliminary observation should be explored further to gain insight in the possible origins when elevated uranium concentrations are observed in the South African water sources.

Conclusions

a Ranking the number of sites according to the proposed guideline dose values from the data provided in Table A shows the following pattern:

Number of sites with:

	Lifetime Average	**12 – 17 years old**	**< 1 year old**
Dose: < 100 μSv/a	34	28	19
Dose: 100 - 250 μSv/a	6	7	13
Dose: 250 - 1000 μSv/a	1	6	8
Dose: 1000 - 5000 μSv/a	0	0	1
Dose: > 5000 μSv/a	0	0	0

Accordingly, it is mandatory to determine the actual use of the water as a drinking water source at those sites showing potentially elevated dose levels, and investigate the possibility to reduce the nuclide concentrations observed in these sources.

b The observed correlation between the uranium concentration (in μg/L) or the gross activity (in Bq/L) and the “all nuclide” yearly dose (in mSv/a) can be used for routine monitoring purposes of the Mooi River catchment area. The estimated uncertainty will be less than 20%. The proposed monitoring frequency is monthly for uranium and every six months for the full range of nuclides to evaluate whether the correlation is sustainable.

c The contribution of radium to the yearly dose estimate is considerable and should be monitored along with the uranium determination for those points were more precise data are required to calculate the yearly dose. The positive correlation between Ra-226 and Ac-227 indicates that monitoring of Ac-227, which has the highest dose conversion factor for ingestion, i.e. the highest radiotoxicity, should be performed on a wider scale.

References

(1) South African Government Gazette, 23 April 1994, Regulation Nr 848, 849

(2) CNS, Annual report 1995/96, Council for Nuclear Safety, Centurion, South Africa

(3) IAEA, Safety Series 115, 1996, Vienna, Austria

(4) CNS, LG 1032, 1997, Council for Nuclear Safety, Centurion, South Africa

(5) GP de Beer, SAIMM Colloquium on mine closure, MINTEK, 1997, Randburg, South Africa

(6) Goldstein, SJ, Health Physics, 1997, Volume 72, pp 10-18

(7) Kronfeld, J. & Vogel, SJ, Earth and Planetary Science Letters, 105, 1991, pp 191-195

Table 1. South African default values for intake via inhalation[4,5].

Inhalation in m^3 per hour Age	< 1 a	1-2 a	2-7 a	7-12 a	12-17 a	> 17 a
Public	0,21	0,21	0,34	0,64	0,96	0,95
Workers						1,2

Dust concentration Environmental: 50 µg/m^3

Workplace: 150 µg/m^3

Table 2. South African default values for intake via ingestion[4].

Consumption per year in kg fresh weight Age	< 1 a	1-2 a	2-7 a	7-12 a	12-17 a	> 17 a
Freshwater Fish	0.5	1	5	10	10	25
Meat	10	20	50	75	100	100
Poultry	7.5	15	35	60	75	75
Eggs	3	6	15	25	30	30
Cereals and Grains	45	60	75	90	128	150
Root crops	51	68	85	102	145	170
Other Vegetables Fruits and Nuts	39	52	65	78	111	130
Water (Litres)	200	260	300	350	600	730
Milk (Litres)	300	300	300	300	300	250

Table 3. Typical values for fresh/dry ratio and specific mass of various foodstuffs.

Matrix		Fresh/dry ratio	Specific mass (g/mL)
Fish	- meat	4,4	0,50
	- bones	3,1	0,59
	- intestines	4.0	0,57
Milk		23,5	0,66
Meat	- bacon	4,5	0,67
	- bone	1,9	0,65
Cereals & grains	- maize	1,2	0,77
Root crops	- potatoes	4.6	0,37

Table 4. Dose conversion factors(3) for ingestion by members of the public (in Sv/Bq)

	< 1 a	1 - 2 a	2 - 7 a	7 - 12 a	12 - 17 a	> 17 a
U-238	3.4E-07	1.2E-07	8.0E-08	6.8E-08	6.7E-08	4.5E-08
Th-234	4.0E-08	2.5E-08	1.3E-08	7.4E-09	4.2E-09	3.4E-09
Pa-234m						
U-234	3.7E-07	1.3E-07	8.8E-08	7.4E-08	7.4E-08	4.9E-08
Th-230	4.1E-06	4.1E-07	3.1E-07	2.4E-07	2.2E-07	2.1E-07
Ra-226	4.7E-06	9.6E-07	6.2E-07	8.0E-07	1.5E-06	2.8E-07
Rn-222						
Po-218						
Pb-214	2.7E-09	1.0E-09	5.2E-10	3.1E-10	2.0E-10	1.4E-10
Bi-214	1.4E-09	7.4E-10	3.6E-10	2.1E-10	1.4E-10	1.1E-10
Po-214						
Pb-210	8.4E-06	3.6E-06	2.2E-06	1.9E-06	1.9E-06	6.9E-07
Bi-210	1.5E-08	9.7E-09	4.8E-09	2.9E-09	1.6E-09	1.3E-09
Po-210	2.6E-05	8.8E-06	4.4E-06	2.6E-06	1.6E-06	1.2E-06
U-235	3.5E-07	1.3E-07	8.5E-08	7.1E-08	7.0E-08	4.7E-08
Th-231	3.9E-09	2.5E-09	1.2E-09	7.4E-10	4.2E-10	3.4E-10
Pa-231	1.3E-05	1.3E-06	1.1E-06	9.2E-07	8.0E-07	7.1E-07
Ac-227	3.3E-05	3.1E-06	2.2E-06	1.5E-06	1.2E-06	1.1E-06
Th-227	3.0E-07	7.0E-08	3.6E-08	2.3E-08	1.5E-08	8.8E-09
Ra-223	5.3E-06	1.1E-06	5.7E-07	4.5E-07	3.7E-07	1.0E-07
Rn-219						
Po-215						
Pb-211	3.1E-09	1.4E-09	7.1E-10	4.1E-10	2.7E-10	1.8E-10
Bi-211						
Tl-207						
Th-232	4.6E-06	4.5E-07	3.5E-07	2.9E-07	2.5E-07	2.3E-07
Ra-228	3.0E-05	5.7E-06	3.4E-06	3.9E-06	5.3E-06	6.9E-07
Ac-228	7.4E-09	2.8E-09	1.4E-09	8.7E-10	5.3E-10	4.3E-10
Th-228	3.7E-06	3.7E-07	2.2E-07	1.5E-07	9.4E-08	7.2E-08
Ra-224	2.7E-06	6.6E-07	3.5E-07	2.6E-07	2.0E-07	6.5E-08
Rn-220						
Po-216						
Pb-212	1.5E-07	6.3E-08	3.3E-08	2.0E-08	1.3E-08	6.0E-09
Bi-212	3.2E-09	1.8E-09	8.7E-10	5.0E-10	3.3E-10	2.6E-10
Po-212						
Tl-208						

Blank data are not available and assumed zero in dose calculations

Table 5 Dose conversion factors[3] for inhalation by members of the public (in Sv/Bq)

	Uptake	< 1 a	1 - 2 a	2 - 7 a	7 - 12 a	12 - 17 a	> 17 a
U-238	S	2.9E-05	2.5E-05	1.6E-05	1.0E-05	8.7E-06	8.0E-06
Th-234	S	4.1E-08	3.1E-08	1.7E-08	1.1E-08	9.1E-09	7.7E-09
Pa-234m							
U-234	S	3.3E-05	2.9E-05	1.9E-05	1.2E-05	1.0E-05	9.4E-06
Th-230	F	2.1E-04	2.0E-04	1.4E-04	1.1E-04	9.9E-05	1.0E-04
Ra-226	S	3.4E-05	2.9E-05	1.9E-05	1.2E-05	1.0E-05	9.5E-06
Rn-222							
Po-218							
Pb-214	S	6.9E-08	5.0E-08	2.8E-08	2.1E-08	1.5E-08	1.5E-08
Bi-214	M	8.7E-08	6.1E-08	3.1E-08	2.2E-08	1.7E-08	1.4E-08
Po-214							
Pb-210	S	1.8E-05	1.8E-05	1.1E-05	7.2E-06	5.9E-06	5.1E-06
Bi-210	M	3.9E-07	3.0E-07	1.9E-07	1.3E-07	1.1E-07	9.3E-08
Po-210	S	1.8E-05	1.4E-05	8.6E-06	5.9E-06	5.1E-06	4.3E-06
U-235	S	3.0E-05	2.6E-05	1.7E-05	1.1E-05	9.2E-06	8.5E-06
Th-231	S, M(2-7)	2.4E-09	1.7E-09	8.0E-10	5.2E-10	4.1E-10	3.3E-10
Pa-231	M	2.2E-04	2.3E-04	1.9E-04	1.5E-04	1.5E-04	1.4E-04
Ac-227	F	1.7E-03	1.6E-03	1.0E-03	7.2E-04	5.6E-04	5.5E-04
Th-227	S	3.9E-05	3.0E-05	1.9E-05	1.4E-05	1.3E-05	1.0E-05
Ra-223	S	3.2E-05	2.4E-05	1.5E-05	1.1E-05	1.1E-05	8.7E-06
Rn-219							
Po-215							
Pb-211	S	6.6E-08	4.8E-08	2.7E-08	2.0E-08	1.5E-08	1.2E-08
Bi-211							
Tl-207							
Th-232	F	2.3E-04	2.2E-04	1.6E-04	1.3E-04	1.2E-04	1.1E-04
Ra-228	S	4.9E-05	4.8E-05	3.2E-05	2.0E-05	1.6E-05	1.6E-05
Ac-228	F	1.8E-07	1.6E-07	9.7E-08	5.7E-08	2.9E-08	2.5E-08
Th-228	F(<7), S(>7)	1.8E-04	1.5E-04	8.3E-05	5.5E-05	4.7E-05	4.0E-05
Ra-224	S	1.2E-05	9.2E-06	5.9E-06	4.4E-06	4.2E-06	3.4E-06
Rn-220							
Po-216							
Pb-212	S	6.7E-07	5.0E-07	3.3E-07	2.5E-07	2.4E-07	1.9E-07
Bi-212	M	1.6E-07	1.1E-07	6.0E-08	4.4E-08	3.8E-08	3.1E-08
Po-212							
Tl-208							

Uptake: The most conservative conversion factors are taken due to fast (F), medium (M) or slow (S) uptake of the chemical compound concerned

Blank data are not available and assumed zero in dose calculations

Table 6 Dose conversion factors(3) for inhalation and ingestion by workers (in Sv/Bq)

		Inhalation		Ingestion	
	Uptake	AMAD		Uptake	
		1 µm	5 µm		
U-238	S	7.30E-06	5.70E-06	F	4.4E-08
Th-234	S	7.30E-09	5.80E-09	M	3.4E-09
Pa-234m					
U-234	S	8.50E-06	6.80E-06	F	4.9E-08
Th-230	M	4.00E-05	2.80E-05	M	2.1E-07
Ra-226	M	3.20E-06	2.20E-06	M	2.8E-07
Rn-222					
Po-218					
Pb-214	F	2.90E-09	4.80E-09	F	1.4E-10
Bi-214	M	1.40E-08	2.10E-08	F	1.1E-10
Po-214					
Pb-210	F	8.90E-07	1.10E-06	F	6.8E-07
Bi-210	M	8.40E-08	6.00E-08	F	1.3E-09
Po-210	M	3.00E-06	2.20E-06	F	2.4E-07
U-235	S	7.70E-06	6.10E-06	F	4.6E-08
Th-231	S	3.20E-10	4.00E-10	M	3.4E-10
Pa-231	M	1.30E-04	8.90E-05	M	7.1E-07
Ac-227	S	6.60E-05	4.70E-05	F	1.1E-06
Th-227	S	9.60E-06	7.60E-06	M	8.9E-09
Ra-223	M	6.90E-06	5.70E-06	M	1.0E-07
Rn-219					
Po-215					
Pb-211	F	3.90E-09	5.60E-09	F	1.8E-10
Bi-211					
Tl-207					
Th-232	M	4.20E-05	2.90E-05	M	2.2E-07
Ra-228	M	2.60E-06	1.70E-06	M	6.7E-07
Ac-228	F	2.50E-08	2.90E-08	F	4.3E-10
Th-228	S	3.90E-05	3.20E-05	M	7.0E-08
Ra-224	M	2.90E-06	2.40E-06	M	6.5E-08
Rn-220					
Po-216					
Pb-212	F	1.90E-08	3.30E-08	F	5.9E-09
Bi-212	M	3.00E-08	3.90E-08	F	2.6E-10
Po-212					
Tl-208					

Blank data are not available and assumed zero in dose calculations

PRESENCE OF TECHNOLOGICALLY-ENHANCED NATURALLY-OCCURRING RADIOACTIVE MATERIALS IN THE CZECH REPUBLIC

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Introduction

NRI Rez participates in the TENORMHARM project within the 5th EU Framework Programme. NRI´s effort is focused on evaluation of NORM inventory (identification of priority areas, detailed studies of technological schemes, measurement of selected materials), assessment of radiation dose and health risks to workers and members of the public and ranking the NORM on the basis of its radioactivity, the quantity of managed material and type of industry and/or process.

The NORMs are present in two general branches:

1) Industries based on imported materials:

- phosphate fertilisers production
- production of titanium dioxide pigments

- oil and gas transport and processing
- production of zirconium refractory materials
- thoriated electrodes manufacturing

2) Industry based mainly on domestic raw materials:

- coal mining and its use
- ground water treatment sludge

Phosphate fertilisers production

During the history of phosphate fertiliser production, various raw materials were utilised - the majority of materials was imported from Russia (Kola apatite) and the other part from several North African countries (Morocco, Algeria, Egypt and others). At the present time, only three major factories ensure the Czech consumption of fertilisers (table 1). The currently used technologies do not produce waste and all by-products are recycled. Nowadays, generally less radioactive raw materials are used such as yellow phosphorus and phosphoric acid imported from Ukraine, concentrate of Kola apatite and AMOFOS (mixture of hydrogen- and dihydrogen ammonium phosphate) from Russia.

Table 1: Phosphate fertilisers producers in the Czech republic.

Factory	Used raw material
FOSFA Comp.	"Yellow phosphorus" (Ukraine)
Synthesia Comp.	Kola-apatite concentrate (Russia)
	AMOFOS (Russia)
Lovochemie Comp.	Kola-apatite (Russia)
	AMOFOS (Russia)

Only the concentrate of Kola-apatite contains non-negligible quantities of U-238, Ra-226 and Th-228 (X0 Bq/kg); but even utilizing this material the resulted annual effective dose of workers does not exceeds the guidance level (1 mSv/year) as confirmed from exposure measurement.

Detailed characterisation of Lovochemie factory was performed, including quantification of selected radionuclides (table 2) and exposure measurements.

Table 2: Gamma-spectrometric analysis of samples from Lovochemie factory.

Radionuclide	Activity [Bq/kg]				
	K-40	Ac-228	Th-228	Ra-226	U-238
Kola apatite	37	115	95	38	64
Insoluble residue	366	435	183	142	190
NPK fertilizer	3626	31	33	12	-

The higher value of K-40 in NPK fertiliser is caused by KCl content.

The effective dose rate was measured between 0.04 and 0.26 μSv/h at various places (natural background - 0.2 μGy/h). The highest values were detected in KCl storage facility and in a place of return of insoluble residue to the main technological stream. The actual measurement of the dust has not been carried out so far. Assuming that the dustiness is not exceeding 5 mg/kg and air inhalation is 2000

m^3/year, the effective dose rate of workers would not exceed 0.1 mSv/year. Therefore, negligible dose could be also expected for the member of the public. Detailed measurements of various deposits incl. Pb-210 and Po-210 content have not been performed, but utilization of relatively low radioactive elements containing raw materials indicates secondary importance of such measurements.

In the FOSFA factory the sample of phospho-gypsum from disused sludge lagoons were collected and measured (Table 3). As assumed the phospho-gypsum (used for production of fertiliser and construction materials) had contained only negligible amount of radioactive elements.

Table 3: Gamma-spectrometric analysis of the sample of phospho-gypsum.

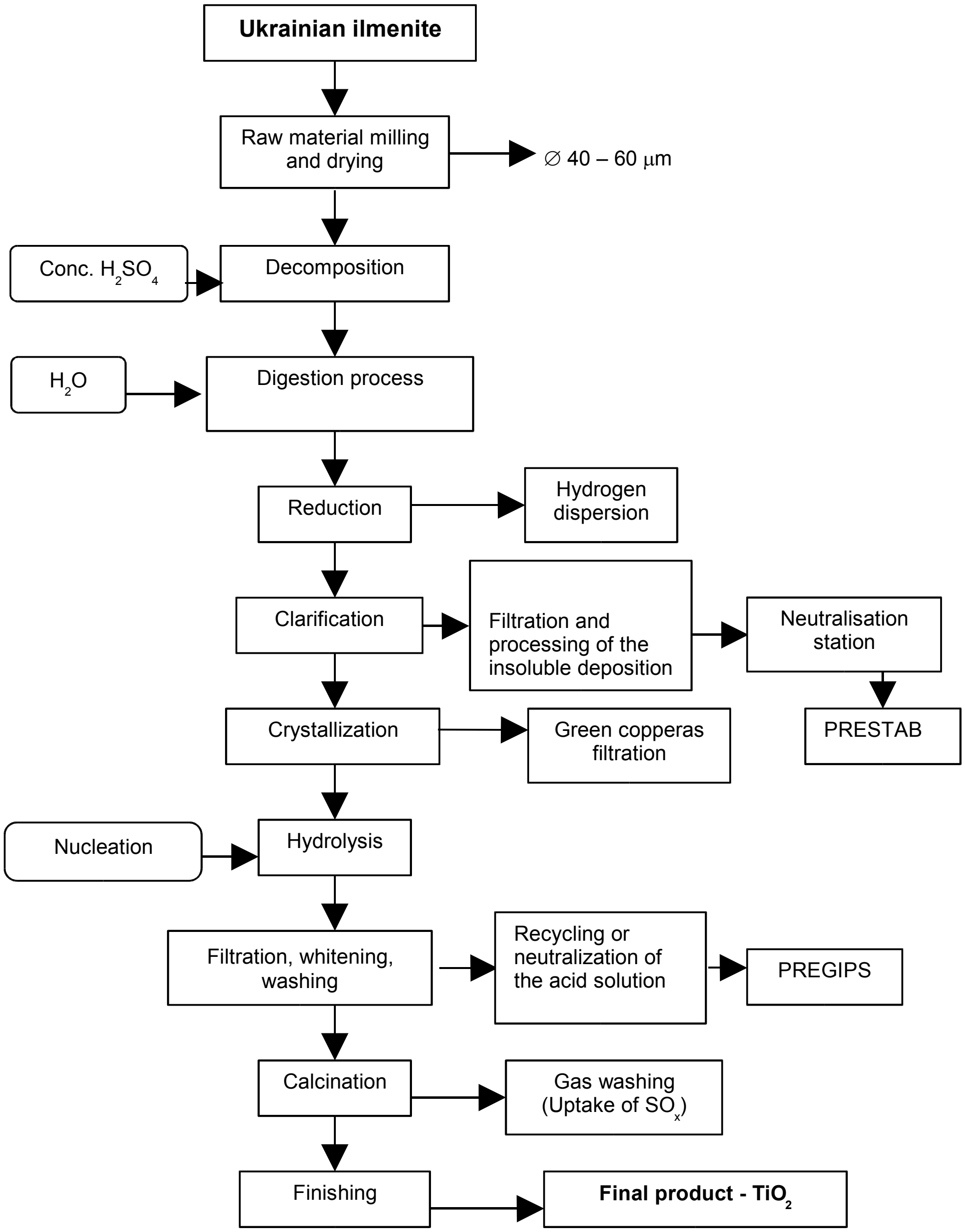
Radionuclide	Activity [Bq/kg]	SD [Bq/kg]	Detection limit [Bq/kg]
K-40	<11.0		11.0
Pb-210	21.7	±2.1	4.0
Ra-226	27.5	±1.1	0.30
Ra-228	28.9	±1.3	1.1
Ac-227	<1.4		1.4
Th-228	32.7	±1.4	0.35
Th-230	<51.0		51
Pa-231	<10		10
U-235	<0.48		0.48
U-238	<4.0		4.0

Titanium dioxide pigments production

Titanium dioxide pigments are produced only in Precheza factory situated in the Prerov town. The capacity of TiO_2 production is at the present time about 65,000 tons per year. This factory formerly used ilmenite imported from Finland, then a mixture of Norwegian and Ukrainian ilmenites (in proportion of 1 : 2, respectively) in 1996 – 2001 period and since 2002 only ilmenite from Ukraine has been used. Ukrainian ilmenite represents a material with relatively high concentrations of uranium and thorium (about 11 ppm of uranium and 20 ppm of thorium); on the other hand the Norwegian mineral contains only about 0.1 ppm of uranium and 0.3 ppm of thorium.

The titanium dioxide manufacture technology is based on digestion of ilmenite with sulphuric acid (“sulphate technology”). Simplified technological scheme is depicted in the Figure 1.

Figure 1: Technological scheme of the titanium dioxide pigments production.



The selected materials from PRECHEZA factory were analysed (table 4) and dose rate was measured in the potentially problematic work areas (table 5) - acquired data were used for the evaluation of radiation risk for workers.

Table 4: Gamma-spectrometric analysis of selected materials from PRECHEZA Comp.

NRPI – laboratory of National Radiation Protection Institute

SONS – laboratory of State Office for Nuclear Safety

Table 5: Dose rate measured at the selected workplaces of PRECHEZA factory.

Workplaces	Dose rate [μSv/h]	Characterisation of the measurement places
LIS-FIKA 310	1.40	Filtration of sludge resulting from clarification (filter press)
Store tank 375	1.00	$TiOSO_4$ solution with addition of PEARLITE, which is used to elimination of residual impurities
LIS-KOFI 377 A,B	1.20 – 1.50	Filtration of residual sludge after addition of PEARLITE
Store tank 417C	2.50	Final solution after hydrolysis – $TiO(OH)_2$ Dose rate in the 1m distance – 1.05 μSv/h
Store tank 417D	3.40	Final solution after hydrolysis – $TiO(OH)_2$
I° MOORE FILTER (empty)	13.0 – 21.0	First step of MOORE filtration after hydrolysis (vacuum filtration)
I° MOORE FILTER (full of $TiO(OH)_2$)	8.00	First step of MOORE filtration after hydrolysis (vacuum filtration) Dose rate in the 1m distance – 3.00 μSv/h

Concerning the storage tanks, there is only low radiation risk for the workers since of their relatively short occupation time there; only in exceptional cases (e.g. during the maintenance activities) radiation risk can be higher. For example, a worker should be present in a close vicinity of storage tank 417D for at least 40 days per year to receive the guidance level dose (1 mSv/year), but such situation is highly improbable. In addition, these tanks are not usually full and therefore the actual effective dose rates are considerably lower. Also the total annual effective dose for an employee working near of LIS-FIKA and LIS-KOFI filter presses does not exceed the guidance level (estimates are 0.87 mSv/year for LIS-FIKA and 0.80 mSv/year for LIS-KOFI). Exception is the situation of an employee working near of vacuum filter (I° MOORE FILTRATION) that can receive the annual effective dose around 14 mSv/year thus considerably exceeding the established guidance level. According to the performed assessments, the filtration equipment serving as the first step of vacuum filtration (which follows after the hydrolysis step - $TiO(OH)_2$) represents a workplace with possible higher radiation risk. The reason are suitable absorption properties of cloth filters in I° MOORE FILTER filtration unit and relatively long periods between their replacements. Due to relatively high cost of used cloth material, the filters are regenerated by concentrated HF. The expected effective dose rate in the vicinity of tanks with this liquor is relatively low (around 0.14 μSv/h) due to the factor of dilution.

The following corrective safety measures are proposed based on performed assessments:

- implementation of personal dosimeter system,
- shortening of the cloth exchange period,
- adaptation of the working time.

The evaluation of selected materials from the point of view of discharge into the environment was also carried out. According to relevant Czech legislative norm (SONS Decree No. 307/2002 Coll.) the clearance level for discharge of natural radionuclides into the environment from the workplaces with possible significantly increased exposure by natural sources is established in the form of the mass activity index derived from the specific activities of K-40, Ra-226 and Th-228 [Bq.kg^{-1}]:

$$I = a_{K\text{-}40}/3000 + a_{Ra\text{-}226}/300 + a_{Th\text{-}228}/200 \qquad (1)$$

The mass activity index would be lower than 2 for unrestricted release to the environment. The mass activity index exceeds twice the clearance level only in the case of sludge from clarification (solid phase) and therefore this material cannot be discharged into environment without approval of State Office for Nuclear Safety. Actually, this material is not directly discharged to the environment - the volume of sludge is firstly reduced by pressing machine and consequently is re-pumped to the neutralisation plant. After neutralisation by lime and calcite the construction material is produced - PRESTAB (brown gypsum with the admixtures of iron oxides). During the sludge treatment the concentration of the radioactivity is decreasing (due to addition of the lime and calcite) and the mass activity index of the PRESTAB product reaches value around 0.8.

Zirconium refractory materials production

Currently, zirconium refractory materials are only processed in Eutit Ltd (Stara Voda town). The melted basalt and the EUCOR are main products of this factory. EUCOR is basically a three-phase system containing 48-50 % of corundum, 30-32 % of badelleyite and 18-20 % of glass phase. The zirconium–containing bricks (with Ra-226 specific activity approx. 1,700 Bq/kg; detail characterisation in table 6) discarded from glass factories are used exclusively for production of EUCOR. The current consumption of approx. 200 tons of zirconium input material means processing of 340,000 kBq of Ra-226.

Table 6: Gamma-spectrometric analysis of used zirconium refractory material.

Radionuclide	Activity [Bq/kg]	SD [Bq/kg]	Detec. limit [Bq/kg]	Radionuclide	Activity [Bq/kg]	SD [Bq/kg]	Detec. limit [Bq/kg]
K-40	107	35	65	**Th-228**	243	10	2.1
Pb-210	214	25	34	**Th-230**	1850	340	180
Ra-226	1680	110	25	**Pa-231**	106	24	4.2
Ra-228	252	13	7.2	**U-235**	76.9	6.2	2.0
Ac-227	87	8.3	5.5	**U-238**	1480	110	15

Coal mining and combustion

The coal exploitation and use represents one of the most important industries concerning NORMs. The coal mining production reached more than 130 millions of tons per year in the past, at the present time decreased to 70 millions of tons. Majority of the exploited Czech coal is used for the energy production. In a process of coal combustion, various radionuclides are concentrated mainly in combustion products - ash, slag and energo-gypsum.

Brown coal mining and combustion:

The most important deposits are situated in the west and north Bohemia - Sokolov basin and North Bohemian basin.

Sokolov basin

The concentration of uranium is 3.1 - 16.3 ppm and thorium 5.0 - 30.2 ppm; activities of relevant radionuclides are included in table 7. The highest thorium concentration (about 30 ppm) were detected in Anezka seam and uranium in Josef seam (15.5 ppm).

Table 7: Activity of selected radionuclides in brown coal from Sokolov basin.

Radionuclide	Activity [Bq/kg]	
Ra-226	30 - 62	46 (average value)
Th-232	<10 - 47	25 (average value)
K-40	<10 - 78	ND

North Bohemian basin

The concentrations of radioelements are lower in comparison with Sokolov basin - uranium 0.5 - 4.1 ppm and thorium 0.2 - 8.9 ppm. The following table contains activities of selected radionuclides in 2 mining areas of the North Bohemian basin.

Table 8: Activity of selected radionuclides in brown coal from North Bohemian basin.

North Bohemian basin	Activity [Bq/kg]		
	Ra-226	Th-232	K-40
Most area	15 – 30	15 – 25	ND
Chomutov area	≤ 20	≤ 10	≤ 10

Uranium and thorium is concentrated mainly in ash and slag as documented in the following table.

Table 9: Content of selected radionuclides and radioelements in brown coal combustion products.

LOCALITY	North Bohemian Coal Co.			Most Coal Co.			Sokolov Coal Co.	
By-products	Ash	Slag	Gypsum	Ash	Slag	Gypsum	Ash	Slag
Ra-226 [Bq/kg]	92.8	66.8	9.2	83.5	69.5	< 4.0	138.5	81.0

Th-232 [Bq/kg]	80.5	63.5	< 9.0	76.5	61.5	< 6.0	92.0	50.0
K-40 [Bq/kg]	324.2	280.5	< 26.0	354.5	288.5	< 13.0	169.2	< 28.0
Uranium [ppm]	7.6	5.5	0.8	6.8	5.7	< 0.3	11.4	6.6
Thorium [ppm]	19.9	15.7	< 2.3	18.9	15.2	< 1.5	22.7	12.3

Hard coal mining and combustion:

The most important basin concerning production of hard coal is Upper Silesian basin situated in the Northern Moravia, other basins are less important. The concentration of uranium in Upper Silesian basin hard coal is between 2 – 9 ppm. Similarly, uranium and thorium is concentrated in ash and slag and gypsum contains negligible level of radioelements as documented in the following table.

Table 10: Content of selected radionuclides and radioelements in hard coal combustion products.

LOCALITY	**Upper Silesian basin**		
By-products	Ash	Slag	Gypsum
Ra-226 [Bq/kg]	128.5	78.0	< 6.0
Th-232 [Bq/kg]	82.0	58.5	< 9.0
K-40 [Bq/kg]	698.5	637.0	< 13.0
Uranium [ppm]	10.5	6.4	< 0.5
Thorium [ppm]	20.2	14.4	< 2.1

Oil and gas exploitation, transport and storage

The majority of oil and gas used in the Czech industries is imported - from Russia (Druzba pipeline) and Norway (IKL pipeline). Measured samples of oil sludge from cleaning of pipelines and from of oil storage tanks revealed only negligible presence of radionuclides (X0 Bq/kg); the similar level of activity has been found in samples from domestic oil exploitation (table 11).

Table 11: Activity of selected radionuclides in oil and oil sludge samples.

Sample	Activity [Bq/kg]									
	K-40	**Pb-210**	**Ra-226**	**Ra-228**	**Ac-227**	**Th-228**	**Th-230**	**Pa-231**	**U-235**	**U-238**
Imported oil transport										
DRUZBA pipeline	<8.70	<3.90	0.75	<1.10	<0.91	<0.35	<27.0	<7.10	<0.30	<2.20
IKL pipeline	<13.0	<4.00	0.32	<1.20	<0.90	<0.33	<38.0	<7.30	<0.31	<2.60
Oil sludge from cleaning of oil storage tank	5.90	47.5	43.1	15.5	<1.20	11.9	<50.0	<10.0	<0.60	<3.50
Oil sludge from cleaning of IKL pipeline	<11.0	60.8	13.4	6.60	<1.20	3.50	<74.0	<10.0	<0.51	<3.10
Domestic oil mining - MND Hodonin Comp.										
Crude oil	<8.60	<2.90	<0.59	<1.32	<1.06	<0.37	<22.9	<5.90	<0.21	<1.59
Purified oil (de-gasification, de-watering)	<7.90	<2.64	<0.53	<1.18	<0.97	<0.34	<22.0	<5.60	<0.20	<1.40
Oilfield water	122	<1.60	<0.30	<0.65	<0.50	<0.20	<12.0	<2.70	<0.11	<0.86
Sludge from oilfield water	243	7.70	55.6	34.4	<2.90	22.2	<51.0	<9.60	<1.70	7.00

Water treatment sludge

State Radiation Protection Institute performed evaluation of radioactivity in sludges resulting from the 68 ground and surface water treatment installations (tables 12 and 13). Significantly higher activities were found in sludge from ground water treatment as can be expected.

Table 12: Gamma-spectrometric analysis results of the surface water treatment sludge.

Nuclide	Number of samples	Arithmetic average [Bq/kg]	Geometric average [Bq/kg]	Maximum value [Bq/kg]
K-40	20	249	128	1330
Pb-210	17	55	41	111
Ra-226	20	21	17	84
Ra-228	20	27	19	103

Ac-227	8	---	---	11
Th-228	20	17	12	61
U-235	6	3.1	2.5	6.5
U-238	15	84	66	354

Table 13: Gamma-spectrometric analysis results of the ground water treatment sludge.

Nuclide	Number of samples	Arithmetic average [Bq/kg]	Geometric average [Bq/kg]	Maximum value [Bq/kg]
K-40	26	158	65	714
Pb-210	32	64	36	208
Ra-226	34	230	93	1290
Ra-228	32	212	87	1102
Ac-227	16	11	11	11
Th-228	34	65	36	316
U-235	17	21	11	66
U-238	21	116	63	425

Conclusion

Most of the Czech industrial companies processing materials with higher naturally occurring radioactivity have been made recently great effort to minimise the potential negative health impacts. The use of some raw materials has been definitely finished, in some cases original raw materials have been replaced by ones with negligible concentrations of radioactive elements (e.g. phosphate fertilisers industry). The coal seams with higher content of radioelements are excluded from mining.

The current assessments indicate that potential radiation risks for workers from processing of NORMs occur during TiO_2 pigments production, but effective doses would be controlled by low cost measures. Higher concentrations of radionuclides were also detected in input material (zirconium-containing bricks) used for production

EUCOR but only around 200 t of this material is processes per year usually during single production campaign and therefore radiation risk is low.

The special problem represents remnants from disused production lines, abandoned milling and chemical processing tailings and dumps or even closed factories. The monitoring, decontamination and disposal of waste from such sites represents important task.

Acknowledgement. The authors thank for partial financial support from EC (TENORMHARM project) and Czech Radioactive Waste Repositories Authority. The authors also appreciate cooperation with the State Radiation Protection Institute and the State Office for Nuclear Safety.

INTERCOMPARISON OF INSTRUMENTS FOR MEASURING RADON AND RADON PROGENY HELD IN the CLOR CALIBRATION CHAMBER*

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Introduction

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Intercomparisons among radon laboratories are of particular importance, because calibrated standards for radon activity concentration and for radon progeny activity concentration in air are not available.

An intercomparison exercise for radon and radon progeny instruments was conducted at the Central Laboratory for Radiological Protection (CLOR) from June 9 to 13, 2003. to verify comparability of mainly continuously measuring instruments for radon and potential alpha energy concentration (PAEC). Seven Polish institutions participated to intercompare ten radon and six PAEC monitors. Radon devices included: six Genitron AlphaGUARD monitors, two Pylon AB-5 monitors and two Polish instruments: RMR1 and a radon probe SRDN2. Among PAEC devices there were five monitors measuring in continuous mode: three T/N Rn WL Meters co-working with AlphaGUARD monitors, Pylon WLx monitor, Radon Progeny Particle Size Spectrometer (RPPSS) designed and manufactured in ARPANSA, Melbourne and one grab sampling device: aspirator SKC equipped with ALFA unit.

Calibration facilities

CLOR maintains a walk-in radon/aerosol chamber with ante-room shown in Fig 1. for use in the quality assurance program for radon and radon progeny measurements.

The chamber body is an air-tight climatized room made of sandwich elements covered inside with stainless steel. Its inner volume is of ca.12.37m^3 and the surface-to-volume ratio of ca. 2.6 m^{-1}. Climatic condition: temperature and relative humidity may be controlled manually or automatically. Temperature may be set up from –30°C to +60°C and relative humidity from 10% to 95% within ±5% (for the temperature range from +10 to +60°C). The chamber contains a radon atmosphere which can be varied from several Bq/m^3 to ca. 52000 Bq/m^3. Radon is delivered from two dry Pylon radium-226 sources, traceable to NIST standards and its concentration is continuously measured by means of one of two AlphaGUARD monitors.

The aerosol conditions in the chamber can be altered as required for studies and calibrations using the TSI water aerosol generator to raise an aerosol level or running of air conditioning engine to lower an aerosol level. The concentration of neutral condensation nuclei is measured by an American condensation nuclei monitor RICH 100.

The concentration of potential α energy (PAEC) in the chamber and the distribution of size of particles-carriers of radon progeny are continuously monitored by means of a unique research tool: Radon Progeny Particle Size Spectrometer (RPPSS) from ACJ&Associates, Inc. designed and manufactured by Stephen B. Solomon in ARPANSA, Yallambie, Australia. This device is considered a reference PAEC monitor.

RPPSS consists of eight stages operated in parallel: one open face stage, 4-stage diffusion battery system and 3-stage inertial impactor system and produces, among others, total PAEC corrected for the loss of the free fraction activity due to the plateout effect in the inlet of the first stage and the distribution of the alpha-active aerosol sizes. The first peak of the distribution corresponds to the free fraction (fp) of particle diameter of ca.1 nm.

The calibration factor converting counts per min. to PAEC expressed in nJ/m^3 is calculated for the average radon progeny alpha particle energy for decays on filter of 7.2 MeV and conversion factor of 1.6 x10^{-13} J/MeV.

The value of the free fraction in the chamber may be altered in the wide range from 0% to ca. 80% and the value of the equilibrium factor F – up to 99%.

CLOR owns also a small 320 dm^3 chamber, which was used as a thoron chamber provided with thoron from a dry flow – through Th-228 source working in the continuous mode.

Description of radon and thoron exposures

Instruments submitted for the intercomparison were placed inside the chamber at 0.5-1.5 m above the floor and started. Radon source was connected to two ports on the opposite sides of the chamber and radon was pumped out into the chamber in closed serial circuit. The total exposure lasted ca. 44 hours and consisted of four intervals, which differed with the relative humidity and concentration of condensation nuclei. In the first interval, continuing overnight, the relative humidity was ambient, of ca. 45%, with the concentration of condensation nuclei becoming lower and lower. In the second interval the relative humidity remained the same and the TSI generator worked injecting aerosols. In the third interval, lasting overnight, the relative humidity was increased up to 95% and the level of aerosols was low. In the fourth interval the relative humidity was high, of 95%, and the TSI generator again injected aerosols to increase their concentration in the chamber.

The radon concentration decreased from ca. 2500Bq/m^3 to ca. 700Bq/m^3 during the whole exposure. The potential alpha energy concentration altered in the range from ca. 1400 nJ/m^3 to ca. 6000 nJ/m^3, concentration of condensation nuclei – from below 200CN/cm^3 to 31000CN/cm^3, equilibrium factor F – from 15% to 99% and free fraction fp – from 0% to ca. 62%. The time courses of radon concentration according to six AlphaGUARD monitors and PAEC according to PAEC meters readings are shown in the Fig.2 and 3. In the Fig. 4 the time course of equilibrium factor F and free fraction fp is illustrated. In the figures the four intervals of interest are marked. Example of particle size distributions for various aerosol conditions during the exposure is given in the Fig. 5.

AlphaGUARD monitors were also compared in atmosphere of toron in small 320 dm^3 chamber. Toron was delivered from the Pylon dry flow-through Th-228 source working in the flow mode, what resulted in lowering of air pressure in the chamber. The activity of the source was 77 Bq. The monitors worked in turn: in the diffusion and flow mode over ca.17 hours each. The background radon concentration in the chamber was ca. 20 Bq/m^3 and the sum of radon and thoron of ca. 65 Bq/m^3.

Results and discussion

After the exposure has been completed the instruments were taken for analysis. Upon analysis the results of the mean values of radon concentration and PAEC and their uncertainties in the four intervals of exposure were sent to CLOR for comparison and evaluation. For AlphaGUARDs values of temperature, relative humidity, pressure and gamma dose rates were also compared.

Results of radon concentration from all devices in four intervals are summarized in Figs. 6 - 9. Two mean values are marked in each of them: one for six AlphaGUARD monitors and the other for all devices together. The means for AlphaGUARDs are within a range from 0.4 % to 4 % showing very good agreement among the monitors in all intervals with the worse one of 4 % in the interval IV. Standard deviations of the means for all instruments range from 1.8 % to 6 % in four intervals. The highest value of 6 % is due to the value for the device Rn 7 strongly differing from others in the interval II i.e. in the high aerosol atmosphere. It can be explained with a filter imperfectly protecting the detector chamber against radon progeny. Unfortunately, the participant didn't report his result in the interval IV, when the aerosol concentration was also high.

To evaluate each device on the base of its results in four intervals a factor of merit was calculated. This factor is defined according to the following formula:

$$\delta_j = \frac{\sum_{i=1}^{n_j} \left| b_{ij} - 1 \right|}{n_j}$$

where: δ_j – the factor of merit of the method "j", b_{ij} – a bias of the particular result "i" against reference value or an average value of several methods (ratios of results obtained with the method "j" to the reference or average value), n_j – number of results obtained with the method "j". The summing over "i" for the method "j" is from i=1 to $i=n_j$. It should be kept in mine that the better the method the lower the factor.

In the Table 1 the factors of merit of the methods calculated against the mean value for all AlphaGUARD monitors are presented. They range from 0.009 to 0.062 among AlphaGUARDs and to the high value of 0.265 for all devices.

Results of thoron concentration measurements from AlphaGUARD monitors working in the diffusion mode summarized in Table 2 reveal significant discrepancies possibly due to low values of measured concentrations.

Mean values of the climatic parameters (rates temperature, relative humidity and pressure) and gamma dose rates readings for AlphaGUARD monitors in six exposure intervals are compared in the Table 3. The biggest scatter of results equal to 9% (14% of the mean) is in the relative humidity. The readings of temperature and pressure do not scatter more than 0,7ºC (2% of the mean) and 2 mbar (0,2% of the mean), respectively.

The results of the intercomparison of PAEC instruments in four intervals are shown in Figs. 10 – 13. Standard deviations of the interval means range from 5.3% to 10.8%. The factors of merit of the methods calculated against the RPPSS readings are given in the Table 4. They range from 0.072 to 0.306.

In order to estimate how big are losses of PAEC attached with the free fraction due to plateout effect in inlet of the devices, the time courses of PAEC were normalized against the maximum value of the PAEC reading for RPPSS which corresponds to the maximum value of the equilibrium factor F equal to 99% and to a very small value of the free fraction fp equal to 3.2%. The normalized time courses for four radon progeny meters are shown in the Fig. 14. In the region of the highest value of the free fraction of 62% the loss of PAEC estimated in the comparison with the RPPSS reading ranges from 44% for the RD 4 meter to 60% for the RD3 meter.

Summary

The results of the intercomparison for radon monitors in the radon atmosphere above 700 Bq/m^3 show quite good coherence except for one which differed considerably from others in the conditions of high aerosols in the interval II. It shows that it is needed to intercompare in high aerosol conditions not only PAEC monitors but also radon monitors.

It should be emphasized that the coherence of radon concentration results in various aerosol and climatic conditions for AlphaGUARDs is very good in the applied range of radon concentration and the factors of merit for them are low: from 0,01 to 0,06. The unsatisfactory results of the intercomparison of AlphaGUARDs in thoron atmosphere of low concentration and low air pressure suggest the need to compare the instruments in the low radon concentration, below 100 Bq/m^3, and to check them in the low air pressure conditions.

The results from the PAEC instruments show bigger discrepancies than ones from radon monitors. It is due to many contributing factors such as: the stability of the flow rate in various climatic and aerosol conditions, the efficiency of the detector system, the integrity of the filter and filter holder and the radon progeny plateout effect upstream dependent on aerosol conditions .

Table 1. Factors of merit for the radon meters.

Radon monitors	Factor of merit
AG 1	0.009
AG 2	0.013
AG 3	0.019
AG 4	0.013
AG 5	0.031
AG 6	0.062
Rn 7	0.265
Rn 8	0.137
Rn 9	0.069
Rn 10	0.154

Table 2. Results for AlphaGUARD's from thoron exposures

AlphaGUARD	Tn concentration Diffusion mode [Bq/m^3]	Tn concentration Flow mode (1 dm^3/min.) [Bq/m^3]
AG 1	57 ± 4	39 ± 4
AG 2	42 ± 3	55 ± 4
AG 3	41 ± 3	-

AG 4	129 ± 7	-
AG 5	92 ± 6	76 ± 5
AG 6	38 ± 2	88 ± 6
Mean ±S.D.	67 ± 15 (22%)	65 ± 11 (17%)

Table 3. Comparison of readings of climatic parameters and gamma dose rate for AlphaGUARD monitors

Interval	Parameter	AG 1	AG 2	AG 3	AG 4	AG 5	AG 6	Max. difference
I	Temperature	31.5	31.6	31.4	31.2	31.7	31.4	0.5
	Relative humidity [%]	46	48	52	46	51	50	6
	Pressure [mbar]	1008	1009	1008	1008	1008	1008	1
	Gamma dose rate [nSv/h]	-	153	142	-	153	-	11
II	Temperature	33.1	33.6	33.1	32.9	33.1	33.3	0.7
	Relative humidity [%]	45	47	51	45	49	49	6
	Pressure [mbar]	1010	1011	1010	1010	1010	1010	1
	Gamma dose rate [nSv/h]	-	153	147	-	153	-	6
III	Temperature	33.7	33.8	33.6	33.6	34	33.8	0.4
	Relative humidity [%]	99	99	99	97	99	99	2
	Pressure [mbar]	1008	1008	1007	1008	1008	1008	1
	Gamma dose rate [nSv/h]	-	150	145	-	152	-	7
IV	Temperature	33.3	33.3	33.3	33.3	33.4	33.7	0.3
	Relative humidity [%]	96	99	99	90	98	93	6
	Pressure [mbar]	1006	1006	1005	1006	1005	1005	1
	Gamma dose rate [nSv/h]	-	154	152	-	151	-	3
Tn diff	Temperature	25.7	25.7	25.2	25.2	25.6	25.6	0.5
	Relative humidity [%]	60	64	68	59	64	63	**9**
	Pressure [mbar]	994	995	995	993	994	994	**2**
	Gamma dose rate [nSv/h]	-	111	117	-	118	-	7
Tn flow	Temperature	26.5	26.7	-	-	26.2	27.3	**1.1**
	Relative humidity [%]	59	59	-	-	61	57	4
	Pressure [mbar]	975	976	-	-	975	972	2
	Gamma dose rate [nSv/h]		107	-	-	119	-	**12**

Table 4. Factors of merit for the PAEC monitors.

PAEC monitors	Factor of merit
RD 1	0.072
RD 2	0.148
RD 3	0.145
RD 4	0.306
RD 5	0.162

Fig.1. Radon chamber at CLOR

Fig. 2. The time course of radon concentration
Comparison of 6 AlphaGUARD's

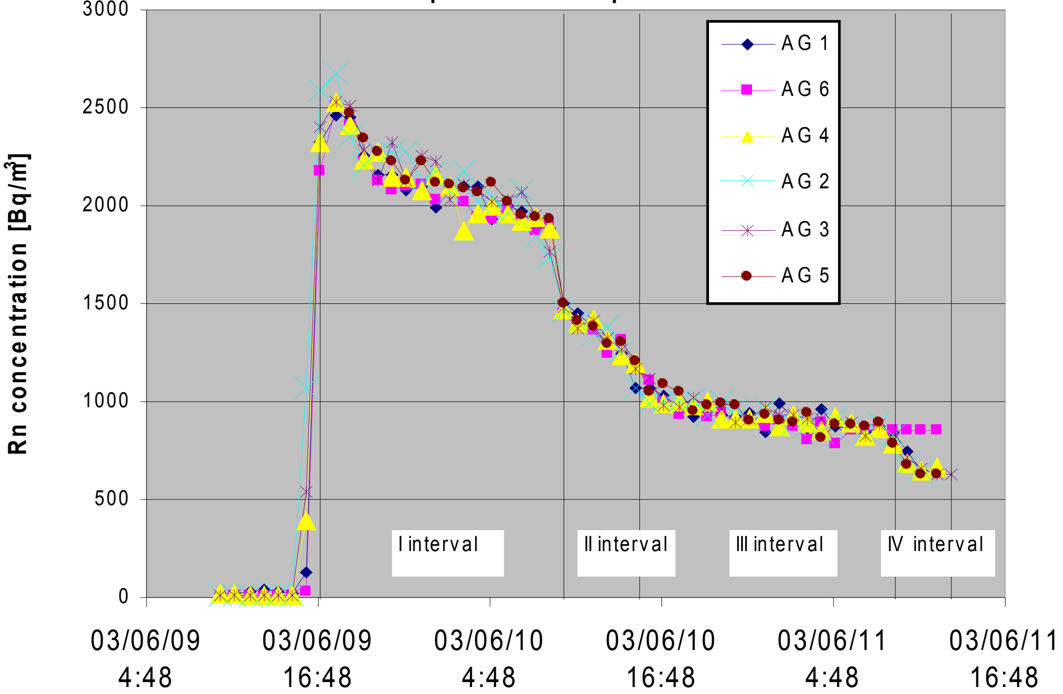


Fig.3. The time course of PAEC readings
Comparison of 5 PAEC monitors

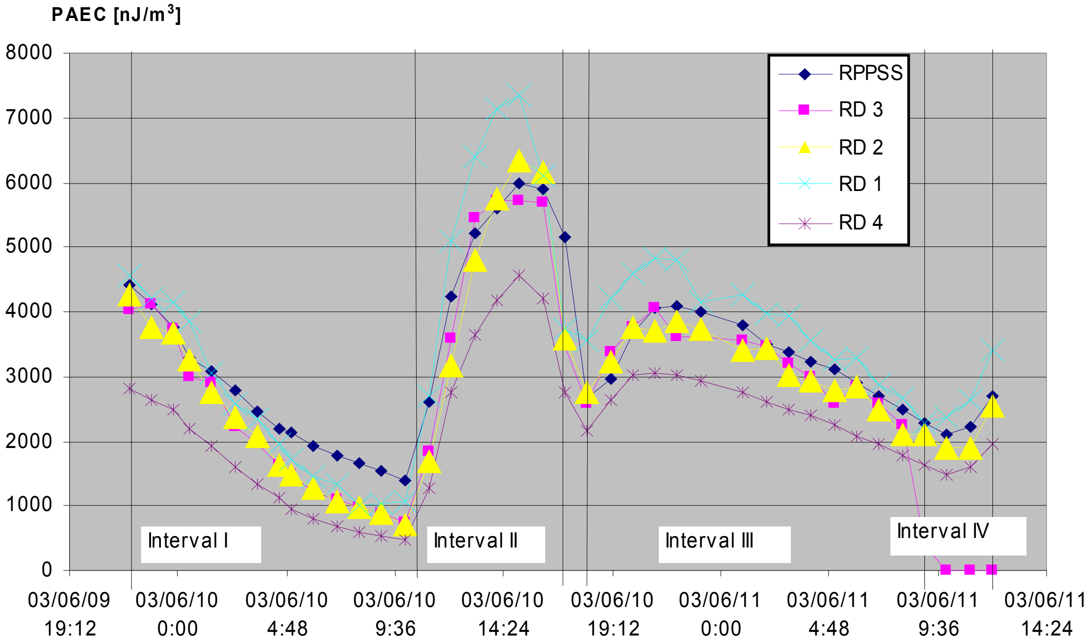


Fig. 4. The time course of F & fp

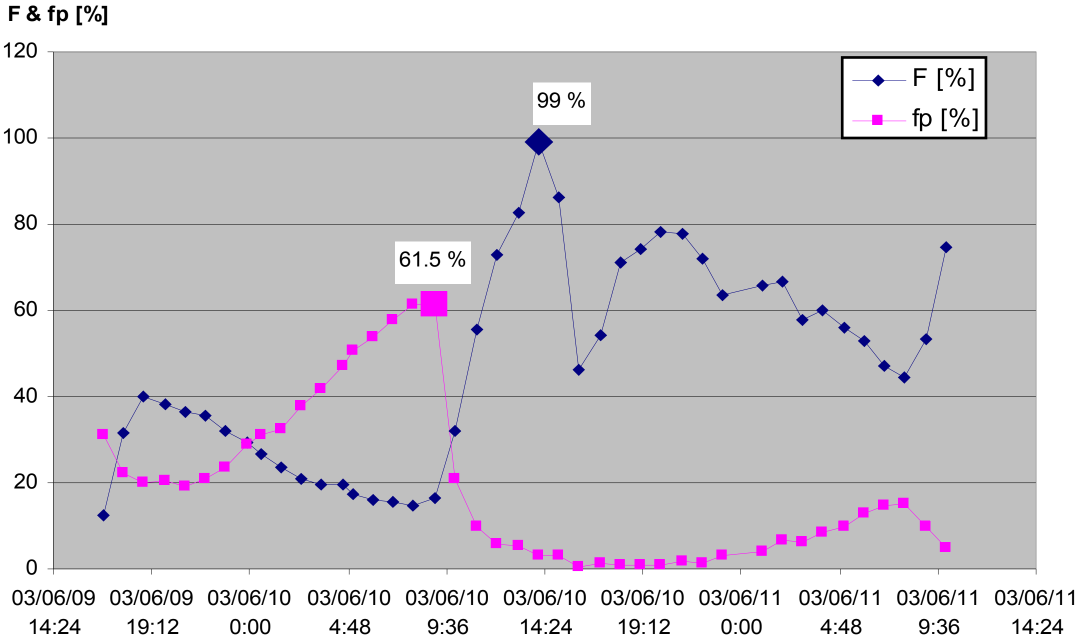


Fig. 5. Particle size distributions for various aerosol conditions

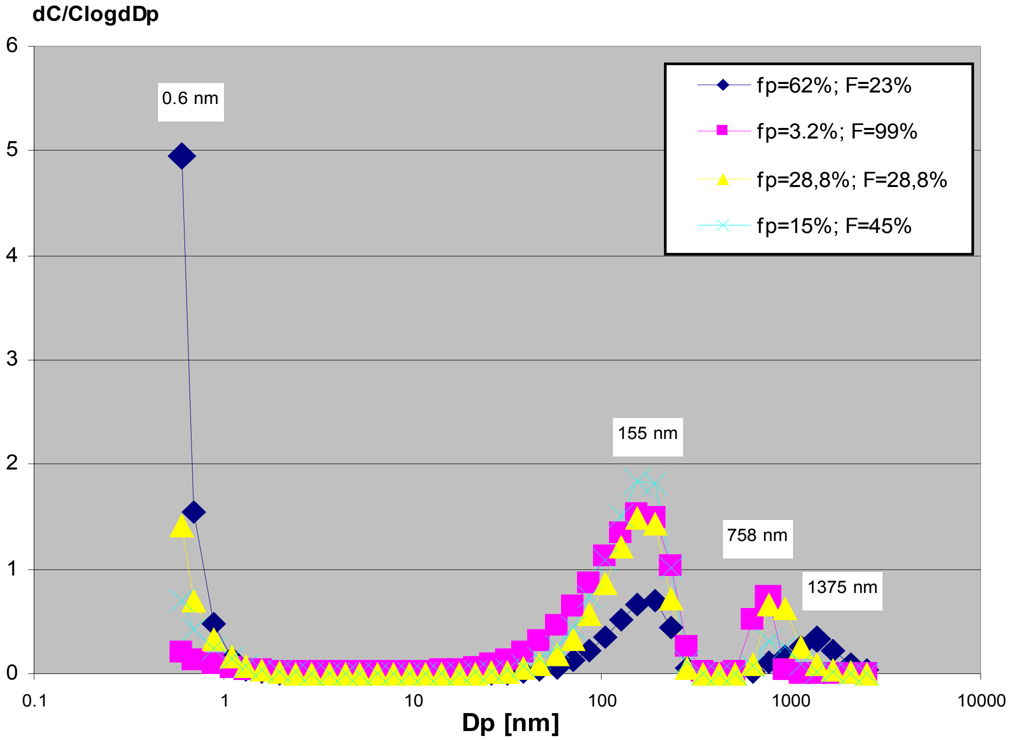


Fig. 6. Radon monitors - I interval (rH=45%, low aerosols)

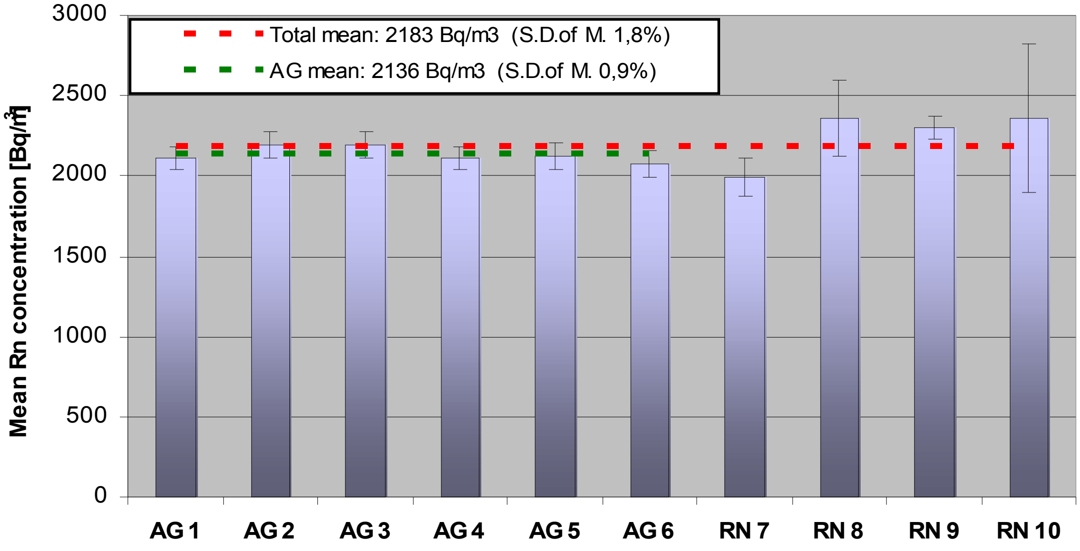


Fig.7. Radon monitors - II interval (rH=45%, high aerosols)

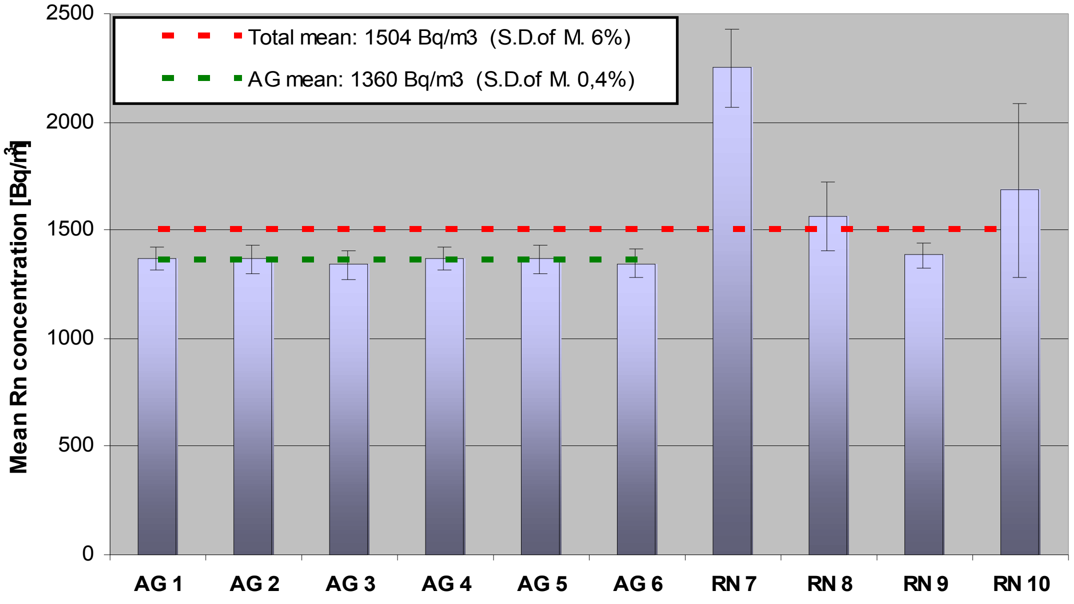


Fig. 8. Radon monitors - III interval (rH=95%, low aerosols)

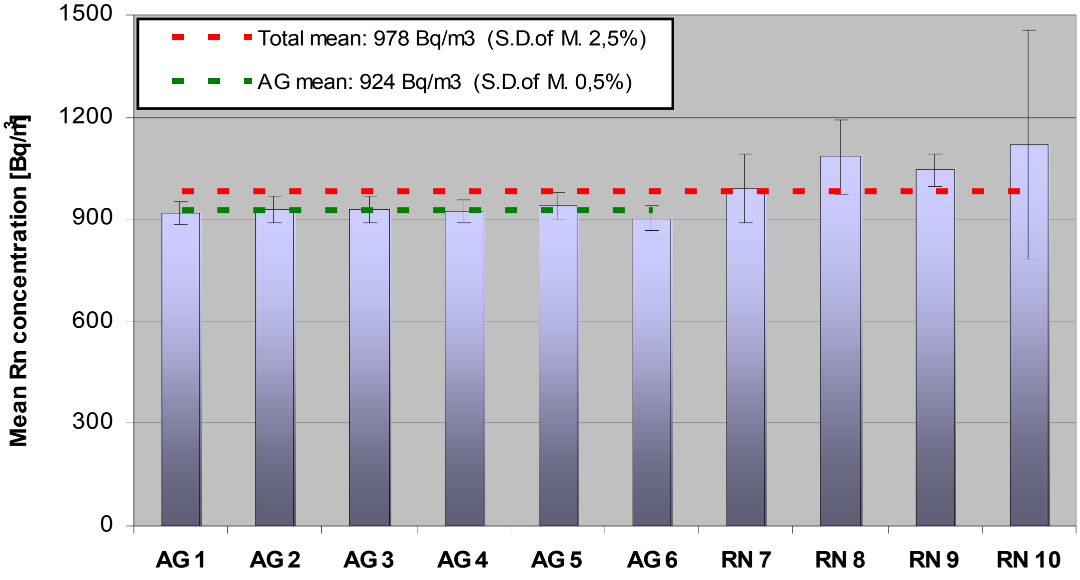


Fig.9. Radon monitors - IV interval (rH=95%, high aerosols)

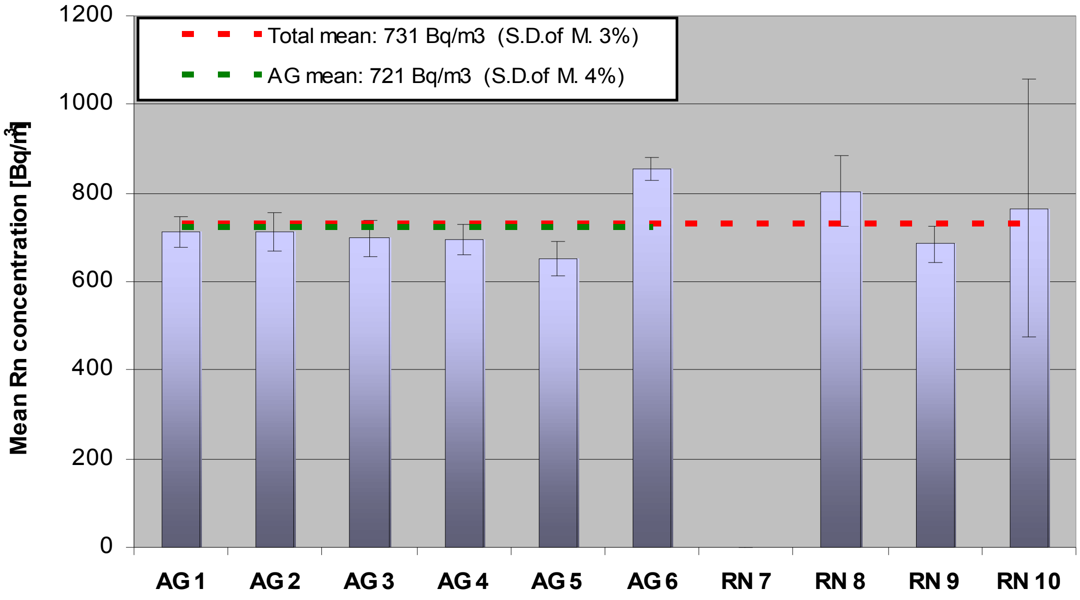


Fig. 10. PAEC monitors - I interval (rH=45%, low aerosols)

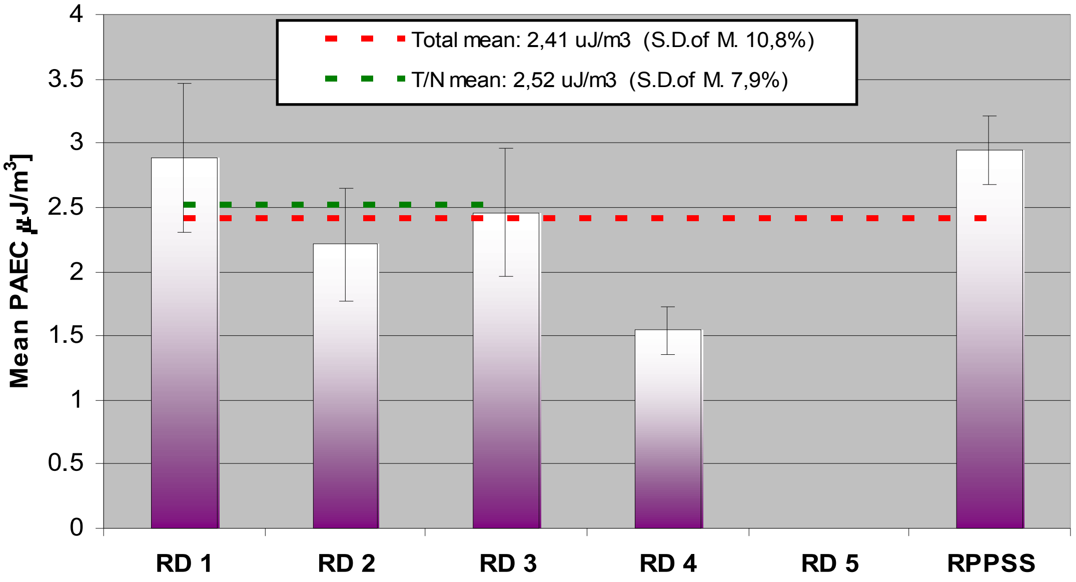


Fig. 11. PAEC monitors - II interval (rH=45%, high aerosols)

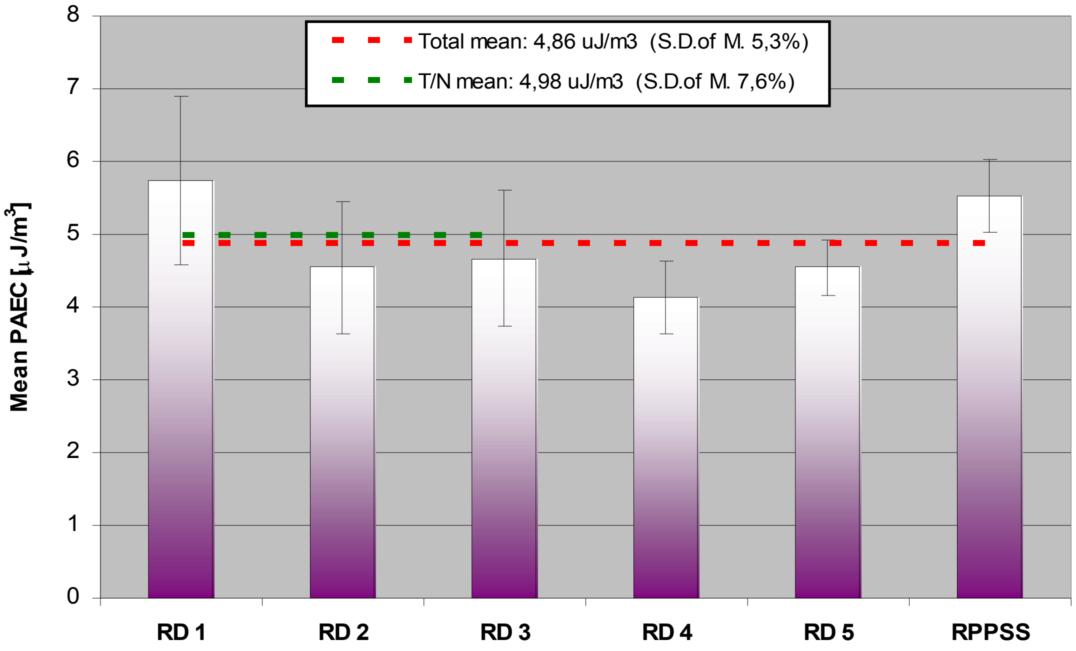


Fig. 12. PAEC monitors - III interval (rH=95%, low aerosols)

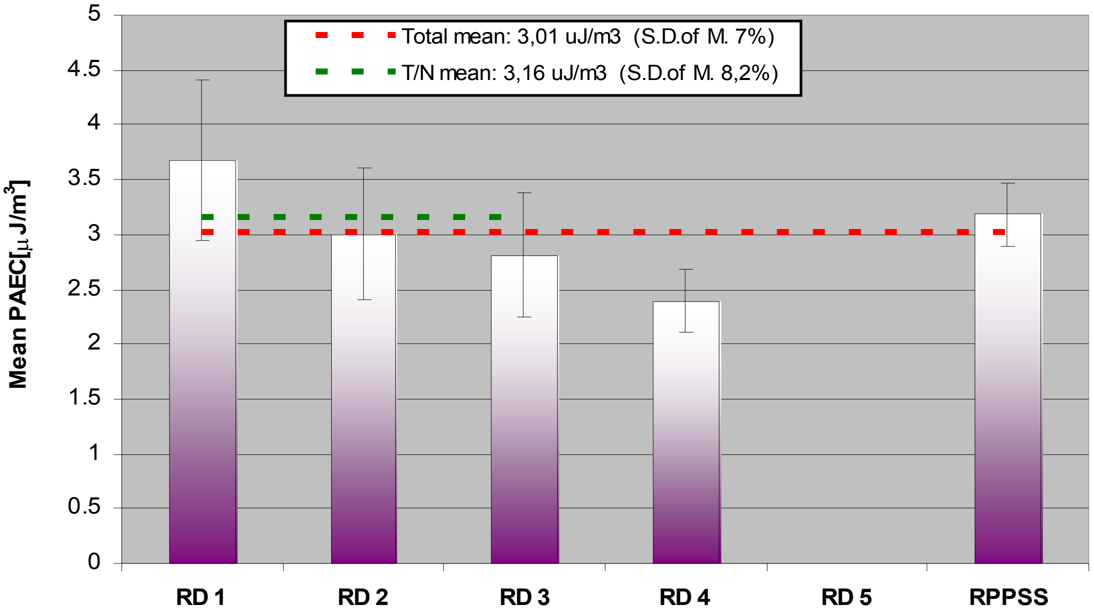


Fig. 13. PAEC monitors - IV interval (rH=95%, high aerosols)

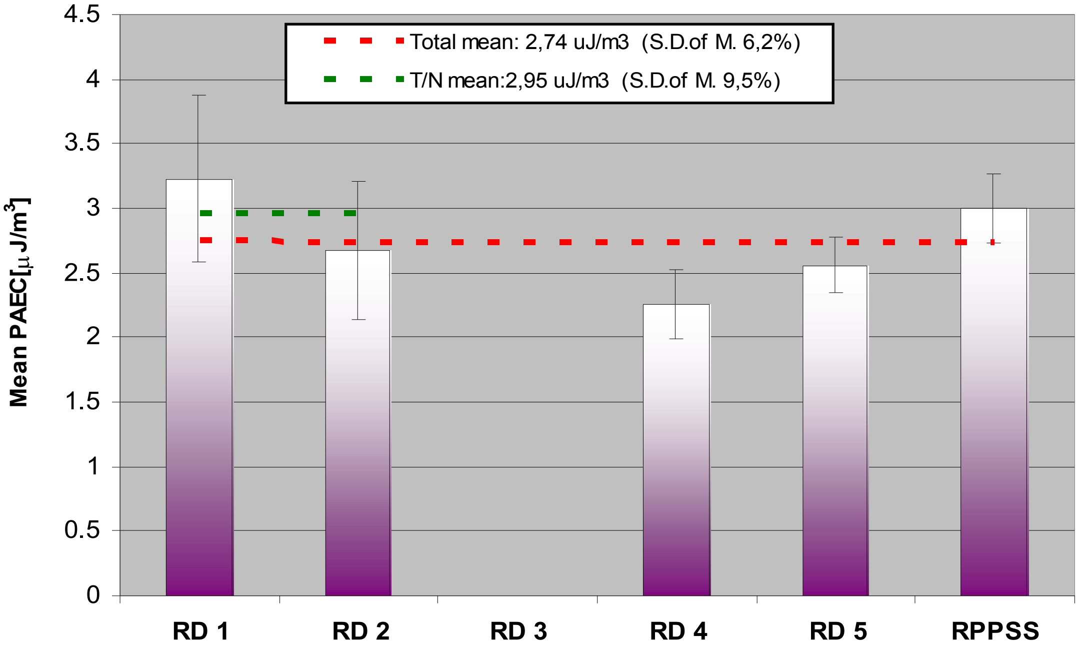
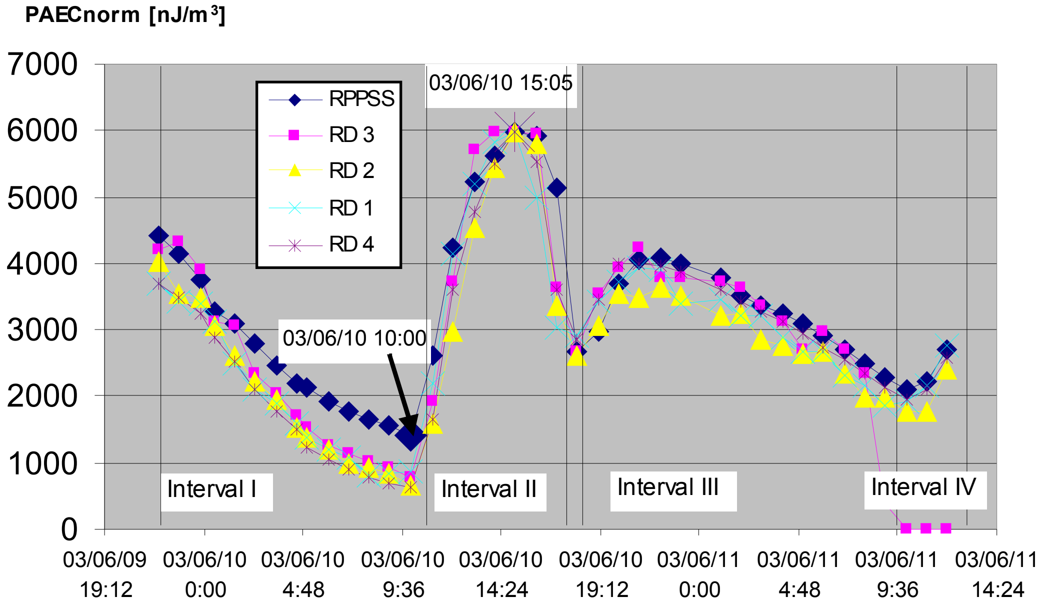


Fig. 14. The time course of PAECresults normalized against RPPSS at 03-06-10 15:05



IDENTIFICATION OF ENHANCED CONCENTRATIONS OF PB-210 AND PO-210 INIRON ORE INDUSTRY

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The German Radiation Protection Ordinance, in place completely since January 2004, contains in Part 3 special regulations regarding recycling and disposal of residues and/or by-products with enhanced natural radioactivity (ENORM). Such material may occur in several industries, for example, in the iron ore industry in by-products of the pig-iron production process. Thus, a study has been initiated to investigate the naturally occurring radioactivity in by-products such as sinter-dust and blast-furnace sludge. The assessment of the radionuclide contents of these materials is important, since about 200000 - 300000 tons of dust and/or sludge are obtained each year at the seven production places in Germany [1] and, depending on the specific activities, a radiation protection control may be required.

The process of converting iron ore into iron centers on the blast furnace. The raw materials, iron ore and other ingredients (sinter, coke, scrap iron) used in the conversion process contain, besides iron, many elements in low concentrations. They are fed into the top of the furnace, and pre-heated air is blown into the base of the furnace to burn the coke and to generate the high temperature needed for the chemical processes. Liquid iron is removed from the bottom, whereas the gas (with dust) passing through is taken off from the top and cleaned to be used, e.g., as fuel. For an optimal operation of the furnace, the raw materials must be in a certain size. However, some material is too fine in size, and thus has to be sintered prior to use. In this sinter process, as well as in the blast-furnace melting and reduction process, the raw materials are heated up to temperatures above 1600 °C. At this high temperature, elements with low melting and boiling points such as lead and/or polonium are vaporized and partly taken out with the hot gas stream. The gas is subsequently cooled down and in this process the volatile Pb and Po atoms get attached to the dust particles inside the gas stream. In the sinter facility, a multi-step dry-air cleaning procedure is applied and a large fraction of the dust particles are recycled as ingredients to the sinter process. The dust from the last cleaning step only is taken out as waste and has been analyzed in our study.

The hot gas from the blast furnace is also cooled down and cleaned in a multi-step process. First, the coarse-grained fraction of the dust which contains large concentrations of carbon and iron is filtered out and recycled into the sinter process. Second, the fine-grained fraction undergoes a special wet-cleaning procedure using water as cleaning substance for the dust particles. Thus, this fraction of the dust is converted into a sludge and contains many elements with low melting and boiling points, i.e. mainly heavy metals such as Zn, Cd, Pb and Po (and hence also radioactive Pb-210 and Po-210) in enhanced concentrations. Even that the concentrations of Pb and Po are very low in the raw materials, the large amount of material used in the pig-iron production process generates a considerable amount of waste which is deposited in authorized and fenced areas. Samples of this sludge have been taken and analyzed too.

In the first step of our study, several samples obtained from the sinter and blast-furnace gas cleaning facilities at one production plant have been investigated. The samples have been analyzed via two different methods: (i) gamma-ray spectrometry and (ii) alpha-particle counting after radiochemical processing of the sample material.

Method (i): The samples have been dried off in an oven at a temperature of about 80 °C only, well below the melting and boiling points of Pb and Po. Subsequently, the material was filled in cylindrical containers made out of aluminum with gas-tight tops to keep the radon and its decay products inside. The containers were stored for about 23 days to achieve a radioactive equilibrium of Ra-226 and its decay products.

The nuclide Pb-210 with a half-life of $T_{1/2} = 22.3$ years undergoes beta decay to Bi-210. During this decay, 84 out of 100 events proceed to the level at 46.5 keV excitation energy in Bi-210, which in turn decay via a 46.5 keV gamma ray to the ground state. Thus, the specific activity of Pb-210 can be directly determined via the measurement of this low-energy gamma transition. We used a well-shielded n-type high-purity Ge detector of about 40 % relative efficiency to detect this gamma ray. A typical measuring time of about 40000 s has been used which is reasonable for our geometry. Special care has been taken to correct the intensity of the 46.5 keV line with regard to the self-absorption in the sample material. For this purpose, a series of measurements with different amounts of sample material has been performed.

Besides the determination of Pb-210, the method of gamma-spectrometry provides also reliable results about the specific activity of many other radionuclides such as K-40, Ra-228, Th-228, Ra-226 and U-238. The contents of these radionuclides were determined as well according to our measuring instructions [2] and the results are given in Table 1. The specific activity of K-40 can be measured directly. In case of Ra-226, the gamma rays associated with the beta decay of the short-lived daughter products Pb-214 and Bi-214 have been analyzed while for the determination of Ra-228 the decay of the short-lived daughter Ac-228 has been studied. To deduce the content of Th-228, the gamma rays accompanying the decay of the short-lived daughter products Pb-212 and Tl-208 were determined, while for U-238, the gamma rays from the decay of the daughter nuclides Th-234 and Pa-234m were analyzed.

Method (ii): The nuclide Po-210 with a half-life of $T_{1/2}$ = 138.4 days is a pure alpha emitter; it cannot be measured via gamma-ray spectrometry. Thus, we have measured the alpha particles after sample preparation via a radiochemical method. The sample dissolution was achieved by treating 100 mg portions with nitric and hydrochloric acids in a first step, and with perchloric acid in a second step. Finally, Po-210 in 0.5 M hydrochloric acid solution was spontaneously deposited in a thin layer on a small nickel disk. The alpha particles emitted from this layer were measured with a calibrated low-background proportional counter. A typical measuring time of 60000 s was used for each sample. The results are given in Table 1.

The measured contents of radionuclides in our samples show remarkably enhanced concentrations of Pb-210 and Po-210. In the sinter-dust samples, the content of Po-210 is about three times higher than that of Pb-210 whereas in the blast-furnace sludge samples the Po-210 content is slightly lower compared to that of Pb-210. The concentrations of the other radionuclides such as Ra-226 or U-238 are within the range expected for normal environmental samples.

Table 1: Typical average values of the measured specific activities of radionuclides in different samples. The activity is given in Bq/kg for dry sample material. The quoted uncertainty (in parentheses) represents a 95 % confidence level (2 sigma).

Sample	**K-40**	**Ra-228**	**Th-228**	**Ra-226**	**U-238**	**Pb-210**	**Po-210**
sinter dust	4000(800)	7.6(1.5)	7.3(1.4)	23(5)	24(6)	15200(2600)	50300(5300)
furnace sludge	280(60)	28(6)	12(3)	74(15)	41(9)	33000(6000)	22200(2500)

To evaluate the mobility of the radionuclides, i.e., the capability to leave the solid material, watery extracts were made according to DIN 38414, Part 4 [3], and analyzed with radiochemical methods. It was shown that about 0.001 - 0.002 % of Pb-210 and Po-210 only are available in an easily leachable form and relevant amounts of radionuclides in seepage water at disposal areas are very unlikely to occur.

As a consequence of the high Pb-210 and Po-210 radionuclide contents, the materials investigated have to be handled according to the regulations outlined in the German Radiation Protection Ordinance, Part 3, §§ 97 – 102, i.e., recycling and/or disposal of these materials are subject to radiation protection control.

A case study has been performed [4] to estimate the dose expected for the workers handling the sludge waste during the disposal process, and for the population living in close vicinity to the disposal area. Several scenarios for possible paths of the exposure have been considered such as external exposition due to gamma radiation, internal exposition due to inhalation of dust, exposition due to direct ingestion of material and exposition due to food produced locally. A possible distribution of the radionuclides via the water paths (surface water, ground water) has been considered too.

The different scenarios for the estimate of the occupational dose of the workers handling the blast-furnace sludge show that the exposure due to inhalation of dust particles is the most important contribution. The reference dose value of 1 mSv per year is not exceeded for the workers as long as the specific activities are below the value of about 50 Bq/g. The expected exposure of a person from the general population is small and can be neglected compared to that of the workers depositing the material. Thus, as long as the specific activities are below the value given above, the material can be released from the radiation protection control by the authorities.

[1] Brenk Systemplanung GmbH: Eingrenzung und Bewertung der von den vorgesehenen NORM-Regelungen der Novelle StrlSchV betroffenen Bereiche, Aachen, Januar 2000.

[2] Meßanleitungen für die Überwachung der Radioaktivität in der Umwelt und zur Erfassung radioaktiver Emissionen aus kerntechnischen Anlagen, Kap. IV.1.4,

Herausgeber: Der Bundesminister für Umwelt, Naturschutz und Reaktorsicherheit, Urban & Fischer Verlag, München, Jena.

[3] DIN 38414 (S4): Bestimmung der Eluierbarkeit mit Wasser, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Schlamm und Sedimente, Weinheim, 1988.

[4] HGN Hydrogeologie GmbH, (R. Gellermann): Radiologische Bewertung der Deponierung von Hochofenschlämmen in der Roheisenerzeugung, Braunschweig, May 2003.

TEST OF THE MATERIAL FOR RADON SEAL LAYER AT THE MINE WASTE DISPOSAL SITE JAZBEC

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Abstract

About 1,4 million tons of the mine waste material was deposited at the mine waste disposal site Jazbec during the uranium ore mining in the uranium mine Zirovski Vrh. The average concentration of uranium in the mine waste is about 60 g/ton, the average specific activity of Radium-226 is 730 Bq/m^3. To reduce the radon exhalation rate and to reduce the penetration of the rainfall water into the waste pile it should be covered with an appropriate material. The surface of the waste pile is about 5 ha. The thickness of the cover should be about 2 m. A test field on the waste pile Jazbec (100 m long and 12-20 m wide) was constructed in the year 2003. The surface of the test field was separated in two parts: one part with a multi-layer cover (5 layers), the second part with only two layers. For the seal layer the fine clayey silt and sand were

used. The measurements of radon exhalation were done on the mine waste material, on the seal layer, on the protection layer and finally on the humus layer. For the radon exhalation measurements the method with charcoal absorbers was applied. The time of exposure was 48 hours. The results of the radon exhalation rates assure that clayey silt and sand mixture is an adequate material to use for radon barrage. The average results of the radon exhalation rates are 50% and more percent lower than the obligatory authorised limit of 0,1 Bq/m^2/s. The results of the water penetration measurements are not as low as it is required by the regulations. The improvement of clayey silt and sand characteristics with bentonite was also evaluated.

Introduction

The Zirovski vrh Uranium mine is located in the north-western part of Slovenia, 35 km west of the capital city of Ljubljana. The facilities consist of the underground mine, several mine waste deposits and the mill tailings site. The mill has already been demolished, the area decontaminated.

The uranium ore deposit was discovered in the year 1960. 22 years later the uranium ore extraction started. The first yellow cake was produced at the end of the year 1984. At the end of June 1990 the production was stopped permanently. In the three decades about 60.000 m of adits, galleries, stopes and shafts, about 2.700.000 tons of rock and 630.000 tons of uranium ore were mined. The average uranium concentration in the ore was about 715 gU/ton.

The mine waste disposal site Jazbec was situated at the main entrance of the uranium mine P-11. About 1,4 million tons of mine waste and red mud has been deposited since year 1982. The average concentration of uranium in the deposited materials was about 60 gU/ton, the Ra-226 specific activity about 730 Bq/kg. The amount of red mud is 48.000 t, specific activity of Th-230 in red mud is approximately 60 KBq/kg. By our plans additional 0,4 million tons of mine waste from other mine deposits, ruins of the demolitions of facilities, contaminated soils will be disposed at Jazbec site till the year 2005. Jazbec disposal site is located in the deep ravine of Jazbec brook. The surface of the disposal site is about 5 ha, the altitude between the lowest and the highest point is 65 m at the moment. [6, 7]

After the depositing of mine waste and material from the decontamination and demolition of the mine surface facilities the surface of Jazbec will be reshaped. After the reshapening of the surface, the whole Jazbec will be covered with about 2 m thick layer of natural material. The main reasons for such cover are:
to assure the stability of Jazbec,
to protect the surface of Jazbec from water erosion (in average 1750 mm of precipitation in the last forty years, max 100 mm per day),
to restrict/prevent the entrance of rain water into the body of Jazbec and to reduce the dissolved uranium, the uranium decay products and the chemical components in the seepage water of Jazbec,
to reduce the radon exhalation from the body of Jazbec into the atmosphere.

In the year 1994 a small test field was constructed on the upper plateau of Jazbec. For the seal layer a special clay from Novo Mesto (150 km away from the uranium mine) was applied. The test field of 200 m^2 was divided in three parts, the thicknesses of the layers were 0,2 m, 0,3 m and 0,4 m. The radon exhalation was measured with the charcoal method (Institute Jozef Stefan Ljubljana). The test measurements confirm that the 0,4 m thick layer of clay reduce the radon exhalation from the mine waste into the atmosphere from 0,8 Bq/m^2.s. to 0,02 Bq/m^2.s. On the basis of the results of the radon exhalation measuring the limit of 0,1 Bq/m^2.s and the multi-layer cover were suggested. In the year 1996 Health Inspectorate assumed this limit for radon exhalation and prescribed it as the authorized limit for Jazbec mine waste disposal site. The structure of the cover and the procedure of its realization were defined in the project for long term settlement of the mine waste disposal site Jazbec. [6, 7]

In the late autumn 2002 the actual construction of the seal layer on mile tailings site Borst was tested. The dimensions of the test field were 100 m x 15 m. The activities started during hard raining, the temperatures were 10°C or less. After one month the testing was temporarily stopped. In April 2003 the test on the test field Jazbec began. The location of the test field was determined on the slope of Jazbec. In the meantime a new proposal for the cover structure was prepared. The test field was divided in two parts:

- the lower part, dimensions of the field 50 m x 12 m, the multi-layer cover of five layers, one of the layers was the drainage layer (project proposal of the cover structure),
- the upper part, dimensions 50 m x 20 m, two-layer cover without the drainage layer, (new proposal of the cover structure).

The local community has opossed the transport of the large amount of building materials through a 1000 year-old town Skofja Loka and the local villages in Poljanska valley. To avoid conflicts with the community the clay material for the sealing layer was substituted with the local material from the location close to Jazbec disposal site. The local material (carnian silty and clayey gravel) was tested in the Building and Civil Engineering Institute Ljubljana. By testing it was established that permeability of this material for water is higher than with clay material. The content of fine fraction is not large enough, but it is possible to improve this deficiency with the addition of a fine material such as the bentonite.

Local materials were tested at the mill tailings site Borst in the year 1996. The construction of the test field was in the rain period, the best local materials were selected for the seal layer (clayey gravel – carnian clayish sandstones/clay sand), the applied materials were technically improved and the results of the radon exhalation rates were also excellent. All conditions for a successful test were assured. The test of the local materials was carried out on a small, flat surface of about 300 m^2. But Jazbec disposal site has a surface of about 50.000 m^2, nearly half of the surface is a steep slope. Is it possible to assure such small radon exhalation rate also at the cover of Jazbec disposal site? The answer is no. Dry weather (no precipitations, high temperatures) is technically more convenient for the construction of the cover layers, but it is difficult to assure the required characteristics of the used material. The appropriate period for the construction of cover layers is from May to October, but in this time the temperatures in Zirovski vrh can be very high and the dry periods without rain very long.

Construction of the test field, preparing for the radon exhalation rate measurements

The construction of the test field of Jazbec disposal site began in December 2002. The original slope of Jazbec was planed, the incline of the slope was reduced to 20°. In the second part of April the construction of the multi-layer cover started. The slope was flattened with a roller, then the seal layer was built in two separate layers with thickness of 0,3 m and 0,2 m. After this the drainage layer followed, then the shielding layer in two separate layers and at the end the layer of humus. The total thickness of all five layers was 2,05 m. The seal and shielding layers were compacted with a stamp foot roller.

After this the two-layer cover on the upper part of the test field followed. On the left part of the test field particular layers (thickness of 0,3 m) were flattened with a bulldozer and then compacted with a stamp foot roller. On the right part of the test field layers were flattened with a bulldozer.

Table 1: The structure of the cover and the thickness of particular layers

Multi-layer cover (project proposal)

Layer	***Thickness***
Vegetation – grass and bushes	
Vegetation layer – humus or soil	0,25 m
Protecting layer – silty gravel (crushed carnian solid sandstone)	0,8 m
Filter layer – sand, gravel or grit	0,3 m
drainage layer – crushed stone	0,2 m
Sealing layer – clay	0,5 m
Waste rock – mine waste	
Total thickness of cover	2,05 m

Two-layer cover (new proposal)	
Layer	Thickness
Vegetation – grass and bushes	
Vegetation layer, locally available soil	0,25 m
Protecting layer, silty gravel (crushed carnian solid sandstone 0/63 mm)	1,3 m
Sealing layer, clayey gravel (separated weathered carnian clayish sandstones/clay sand)	0,5 m
Total thickness of cover	2,05 m

Daily temperatures during the test were between 20°C and 35°C. To avoid the loss of moisture in the gravel, the gravel was transported directly from the place of the excavation to Jazbec test field. The moisture in the seal layer was in average 15% (11% – 19%). The seal and shielding layers were moistened with water after the compaction. The measurements of radon exhalation were organized on the next morning. The placing of charcoal canisters started at 6^{30}. For each plastic cylinder a small plateau with dimensions 0,15 m x 0,15 m was prepared. The contact between the plateau and the cylinder was tightened up with clayey material. About 0,3 m above the plateau a cross channel with the length of 0,5 m was hollowed out to take away the surface water in case of rain. In the early afternoon the nearest surrounding of each measuring point was moistened with water to avoid the originating of cracks in the ground caused by dry weather. After this test we substituted moistening of the surface layer with a 3 – 5 cm thick layer of fine, not compacted clayey gravel. A thin layer of gravel or other material is more appropriate than the moistened one.

Measuring methods

A simple method for measuring radon-222 exhalation from the surface was used. It consists of placing the activated charcoal canisters on the ground to adsorb the emitted radon gas from the soil [1, 2, 3, 4]. By using this method, problems caused by back diffusion and leakage are largely eliminated because the activated charcoal virtually adsorbs all the radon entering the exhalation container. Variations of atmospheric pressure in time of exposure have a big influence on the radon exhalation rate [5] and cause its changes. This method gives as a result the average value of the radon exhalation rate for the exposure time used.

Canisters are made of metal with the diameter of 9 cm, 3 cm high and filled with 100 g of charcoal. The charcoal was activated by heating the can, open end up, on an electric fry pan for at least 4 hours at about 150 °C. The cans were sealed with caps and adhesive tape.

Opened canisters were fixed to the ground surface simply by pushing the rim of an outer protective plastic shell into the soil to a depth of about 1cm. The canisters were recovered after the period of two days and resealed with their metal caps. They were then left for a period of at least 3 hours to allow the radon daughters to grow towards the equilibrium with radon.

Counting was done inside a lead-brick shield to reduce the background from external radiation. The gamma activity of the canisters was measured using high purity Ge detector on multichannel analyser system. Three gamma peaks of radon daughters were used for analysis: 295 keV and 352 keV of ^{214}Pb and 609 keV of ^{214}Bi. The efficiency of the detector for charcoal canisters has been determined using the reference charcoal canister from Isotope Products Laboratories, Source no. 236-4-5-8 filled with the standard radium solution in the radioactive equilibrium between radon and radium.

The results of the radon exhalation measurements

The geophysical measurements as measurements of material compression showed, that it is not possible to assure the same geomechanical characteristics in the layer at the steep slope as at the flat surface. But at the thickness of the cover of 2 meters this deficiency does not have a measured influence (impact) on radon to pass through the seal and shielding layers. The average measured radon exhalation rates on the different layers were lower as the obligatory authorised limit of 0,1 Bq/m^2.s is. In June this year the new series of measurements will be performed to check the radon exhalation rates after one year of the existence of test field Jazbec.

The results of radon exhalation measurements on diferent types of layers and with different thicknesses of layers are presented in table 2.

Table 2: Average radon exhalation rates on the testing field of the disposal site Jazbec

Type of layer, thickness of layer	Average radon exhalation rates Bqm^{-2}s^{-1}	Effect of the covering layer (%)
Mine waste, covered with 0,1 – 0,25 m thick layer of soil	1,19	21
Mine waste, planed with a bulldozer, compacted with a stamp foot roller	1,50	0
Sealing layer, clayey gravel, thickness of 0,5 m, flattened with bulldozer, compacted with stamp foot roller, lower test field	0,02	99
Drainage layer, grit, thickness of 0,2 m, + filter layer, grit, thickness of 0,3 m, + protecting layer, crushed silty gravel, thickness of 0,8 m, flattened with a bulldozer, compacted with a stamp foot roller, the lower test field	0,05	97
Sealing layer, clayey gravel, thickness of 0,5 m, flattened with a bulldozer, minimally compacted with a stamp foot roller, left part of the upper test field	0,08	95
Sealing layer, clayey gravel, thickness of 0,5 m, flattened with a bulldozer, not compacted with a stamp foot roller, right part of the upper test field	0,05	97
Protection layer, crushed gravel, thickness of 1,8 m, flattened with bulldozer, not compacted with stamp foot roller, upper test field	0,04	97
Final covering with humus, deposited and flattened with an excavator	0,07	95
Obligatory authorised limit	0,1	93

To reduce the flow of radon from the mine waste layer through the cover layer the preservation of moisture in the gravel before built-in and compression is of large importance. This statement was confirmed at Borst test field, built in the year 1996. The seal layer (0,5 m thick, clayey gravel) was not protected with an additional shielding layer. During the seven winters (frost) and seven summers the clayey gravel broke up. The radon exhalation rates, measured in dry weather in September 2003, were a few hundred times larger than during the rainy autumn in the year 1996. [6, 7]

The conclusion

The results of the radon exhalation rates assure that clayey gravel is an adequate material to use as the radon barrage at Jazbec mine waste disposal site. The thickness of 0,6 m of clayey gravel is enough to reduce the radon flow under the required value. The efficiency of such type of a layer is higher, if the clayey gravel is compacted intensively and if the layer is built-in in several thin layers. It is very important to keep the natural moisture in the clayey gravel at the built-in procedure and to put the protection layer as soon as possible on the sealing layer to protect the drying of gravel.

On the basis of the radon exhalation rates from Jazbec disposal site the contribution of radon to environment is estimated up to 2 TBq Rn-222/year. After the cover of Jazbec is finished the contribution of radon will be about 0,2 TBq Rn-222/year. The additional contribution of the radon from mine waste to the radon concentration at Jazbec area is estimated < 10-20 Bq/m^3.

The method with the charcoal canisters is adequate to use for radon-222 exhalation. The deficiency of this method is sometimes the time of sampling (48 hours). No other activities are allowed at the same time in the surrounding. In time of the sunny weather and the higher temperatures is very important to control the originating of cracks in the ground in the nearest surrounding of measuring points. To prevent the surface of layer from cracks the moistening with water or 3-5 cm thin layer of clayey gravel have been used in Zirovski vrh.

The two-layer cover will replace the multi-layer cover at Jazbec mine waste disposal site and at the mill tailings site Boršt. The reasons for such decision are the following:

- the two-layer cover is much easier to construct than the multi-layer cover,
- the stability on the steep slope with a two-layer cover is much higher than with a multi-layer cover,
- the damaging of the two-layer cover is very easy to repair, with the multi-layer cover the repair is of great pretension,
- the maintenance of the two-layer cover is more simple, rare and much cheaper as it is with the multi-layer cover,
- the radon exhalation rates with the two-layer cover are the same as with the multi-layer cover.

A new project for the long-term settlement of the mine waste disposal site Jazbec will be prepared in May 2003. The structure of the cover is shown in table 3.

Table 3: The structure of the cover of the mine waste disposal site Jazbec

Mono-material cover proposed)	
Layer	Thickness
Vegetation – grass and bushes	
Vegetation layer, locally available soil	0,25 m
Storage (interim) layer, crushed silty gravel (carnian solid sandstone 0/63 mm)	0,5 m
Protecting layer, crushed silty gravel (carnian solid sandstone 0/63 mm)	0,8 m
Sealing layer, clayey gravel (separated weathered carnian clayish sandstones/clay sand)	0,5 m
Total thickness of cover	2,05 m

References

1. E. Stranden, A. K. Kolstad: Radon exhalation from the ground; method of measurements and preliminary results, The Science of the Total Envir., 45, p.165-171, Elsevier, Amsterdam, 1985.
2. Megumi, K., Mamuro, T.: A Method for Measuring Radon and Thoron Exhalation from the Ground, Journal of Geophysical Reseearch, Vol 77, 3052 - 3056, 1972.
3. Countess, R. J.: 222Rn flux measurement with a Charcoal Canister, Health Physics 31, 455,1976.
4. Mason, G. C.: A Study of Radon Emanation from waste Rock at Northern Territory Uranium Mines, ARL/TRO44, 1982.
5. A. Janssens at all: Transients in the exhalation of radon caused by changes in ventilation and atmospheric pressure, Proce. Of an Int. Sem. , Anacapri (Italy), 3-5. Oct. 1983, Rad. Prot. Dos., Vol. 7, No. 1-4, p. 81-86, Nuc. Tech. Pub., 1987.
6. M. Krizman: Determination of the parameters for the settlement of the mine waste disposal site Jazbec, Ljubljana, June 1994
7. J. Rojc: Report on measurements of the ionizing radiation in time of the construction of the test field at mine waste disposal site Jazbec, Todraz, June 2003

ESTIMATION OF RADON DOSE IN SEVERAL WORKPLACES USING DOSIMETRIC MODEL FOR INHALATION OF AIRBORNE RADIONUCLIDES

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Introduction

Deposition of inhaled short-lived radon progeny in the respiratory tract is a main source of the radiation dose from exposure to radon. The dose is calculated as a product of the potential alpha energy concentration (PAEC) and a dose conversion factor (DCF).

There are two approaches to the estimation of the DCF (dose per unit intake). One of them, based on the Publication 65 ICRP (International Commission on Radiological Protection) [1] using a single dose conversion factor called conversion convention, is derived from the results of the epidemiological studies of uranium miners. However, the extrapolation from the lung cancer risk for uranium miners applied to the general population meets many objections related to two reasons: big difference of about 2-3 orders of magnitude in the radon exposure, and differences in the exposure environments (e.g. concentration, size distribution and chemical composition of aerosols), breathing rates, smoking pattern and so on. The second approach is based on the ICRP Publication 66 [2] which strongly recommends the usage of dosimetric models for inhalation of airborne radionuclides. These models reveal that the dose per unit intake of radon progeny depends on the site of particle deposition in the respiratory track, which, in turn, strongly depends on the particle size distribution. It is particularly important in the estimation of the dose to take into account the contribution of the ultrafine particles below10 nm in diameter. To recapitulate, for the reliable estimation of the radon dose it is necessary to know not only the potential alpha energy concentration (PAEC), but also the size distribution of radon progeny particles in the range from 1 to 1000 nm, which penetrate to our lungs with the air. The dosimetric model approach uses a weighted dose conversion factor, which combines radon progeny size distribution with the particle-size dependent dose conversion factors in a particular exposure location.

Radon Progeny Particle Size Spectrometer

CLOR owns a unique research tool Radon Progeny Particle Size Spectrometer (Fig.1), manufactured by Stephen Solomon in ARPANSA, Melbourne, Australia, which allows to estimate radon dose with use of the dosimetric model for inhalation of airborne radon progeny.

RPPSS comprises 8 stages operated in parallel: one open face stage, 4-stage diffusion battery system and 3-stage inertial impactor system. In the diffusion battery system filters are preceded by wire screens with increasing numbers: 1, 2, 13 and 32 and mesh 100,100,100,200 respectively in the consecutive stages. In the 3 impactor stages aluminized mylar foil is used as collector. The activity collected on filters and mylars are counted simultaneously by silicon detectors mounted adjacent to them.

The counts are processed by deconvolution analysis for 43 size ranges between 0.60 nm and 2493.9 nm. It is done by means of two different algorithms: the Twomey non-linear iteration [3] and the expectation maximization method described by Maher and Laird [4]. In the continuous mode the deconvolution yields particle size distributions for overall Rn-222 daughters. RPPSS produces among others the following data: total PAEC, distribution of PAEC for 8 stages, unattached fraction defined as the smallest particles collected by the stage No2, distribution of alfa-active aerosol sizes with information on each peak (activity median diameter, percentage contribution and geometrical standard deviation), size-weighted dose conversion factors (for an adult male with a breathing rates of 1.2 m^3/h and 0.78 m^3/h) derived from the ICRP66 Respiratory Tract Model implemented in the computer program RADEP (RAdon Dose Evaluation Program)[5]. Dependence of the dose conversion factors (DCF) on the particle diameters applied in the software of RPPSS is shown in Fig. 2. It reveals that for particle diameter (AMTD) of 2,9nm (the free fraction) the values of DCFs are ca. 22 times higher than for particles of ca. 500nm (the attached fraction). The RADEP-derived values of DCFs are adjusted by a factor of 0.3 to provide consistency with the results derived from the epidemiological risk estimate with the use of the ICRP65 conversion convention.

Collection efficiency curves for all eight stages, in the range of diameters from 0.6nm to 2494nm, applied in the RPPSS software are shown in the Fig. 3.

Measurements and results

Measurements of potential alpha energy concentration (PAEC) and radon progeny size distribution were performed with the Radon Progeny Particle Size Spectrometer at four workplaces: an attorney office with elevated radon level, Faculty of Physics at the Warsaw University, the Central Laboratory for Radiological Protection and an experimental coal mine “Barbara”. The measurements were conducted in two conditions of aerosols: natural and enhanced level aerosols from smoking cigarettes.

Simultaneously, radon concentration was measured with AlphaGUARD monitor to estimate the equivalent factor F.

In the Table 1 data on average radon and potential alpha energy concentration, equivalent factor F and free fraction fp in both: natural conditions and atmosphere of smoking cigarettes at investigated workplaces are summarized. In the “Barbara” coal mine the measurements were performed twice (on two days), both in natural conditions, which are characterized by high aerosol level. The free fraction ranges from 0.3% in high aerosol conditions at CLOR bunker to 30% in the attorney office (computer server room) in low aerosol level due to air conditioning. In the “Barbara” mine the free fraction is at the level of ca.5% with the high value of the equivalent factor F of 74%-89%.

In the Table 2 data on the peaks in the particle size distributions: particle diameter, geometric standard deviation and percent contribution to the total PAEC are given. Examples of measured full distributions of particle size are shown in the Figs. 4a and 4b. In the “Barbara” mine an additional ultrafine particle peak of 7.9 nm occurs.

To estimate the annual effective doses both approaches were applied: the epidemiological with use of the ICRP65 convention conversion (1.425 Sv/(J*h*m^{-3}) for occupational exposure and 1.1 Sv/(J*h*m^{-3}) for environmental exposure) and the dosimetric which is based on the size-weighted dose conversion factors for each particle size distribution. The doses were calculated for an adult male with a breathing rates of 1.2 m^3/h and 0.78 m^3/h, respectively to occupational and environmental exposure, and are compared in the Table 3. Ratios of the doses estimated by the dosimetric model to ones estimated with the use of the single conversion convention range from 0.5 when the free fraction is ca. 5% to 1.7 when the free fraction is ca.30%. Similar results were obtained by S.Solomon in the Fairy Cave, Buchan, Victoria, Australia in the studies performed with the use of his Effective Dosimeter. In this case the underestimation of the effective dose calculated according to ICRP65 conversion convection reached a factor of 2 [6].

Bibliography

[1] International Commission on Radiological Protection (ICRP) Publication 65, 1993; “Protection against Radon-222 at Home and at Work”.

[2] International Commission on Radiological Protection (ICRP) Publication 66, 1994; “Human Respiratory Tract Model for Radiological Protection”.

[3] Twomey, S. 1975; “Comparison of constrained linear inversion and iterative algorithm appllied to the indirect estimation of the particle size distribution”, J.Comp. Phys. 18:188-200.

[4] Maher, E.F. & Laird, N.M. 1985; “Algorithm reconstruction of particle size distributions from diffusion battery data” J.Aerosol Sci. 16:557-570.

[5] Biechall, A. & James A.C. 1995; “Uncertainty analysis of the effective dose per unit exposure from radon progeny and implications for ICRP risk-weighting factors”. Radiat. Protect. Dosim. 60(4):321-326.

[6] Solomon S.B. 2001; “Field tests of a radon progeny sampler for the determination of effective dose” The Science of the Total Environment 272:303-313.

Table 1. Data on Rn-222 concentration, PAEC, equivalent factor F and free fraction fp at investigated workplaces.

Place	Aerosol conditions	^{222}Rn [Bq/m^3]	PAEC [nJ/m^3]	F [%]	fp [%]
Attorney office	natural	1407	614	8	30
	cigarette	1400	1410	18	19
UW Hoża pavilion	natural	224	39	3	10
	cigarette	426	216	9	0.8
CLOR bunker	natural	118	430	65	5.8
	cigarette	102	460	81	0.3
“Barbara”	natural	971	4040	74	5,3
	natural	915	4550	89	5,3

Tabel 2. Data on on the peaks in the particle size distributions: particle diameter (AMTD), geometric standard deviation and percentage contribution of the peak to the total PAEC.

		Peak#1	**Peak#2**	**Peak#3**

Place	Aerosol conditions	**[nm]**	**GSD**	**[%]**	**[nm]**	**GSD**	**[%]**	**[nm]**	**GSD**	**[%]**
Attorney office	natural	0.6	1.16	30	153	2.07	70	599	1.36	1.3
	cigarette	0.6	1.15	19	141	1.76	80	655	1.3	2.5
UW Hoża pavilion	natural	1.0	1.66	10	151	1.49	80	721	1.19	9.7
	cigarette	1.4	1.82	0.5	152	1.51	88	713	1.23	11
CLOR bunker	natural	0.92	1.55	5.8	160	1.54	80	755	1.35	14.2
	cigarette	1.0	1.71	0.3	170	1.38	90	711	1.20	9.5
“Barbara”	natural	0.7	1.33	5.3	131	2.0	83	622	1.22	12
	natural	0.7	1.33	5.3	135	1.87	81	681	1.25	14

Tabel 3. Comparison of annual (8700h) effective doses estimated for an adult male with a breathing rates of 1.2 m^3/h (Occ) and 0.78 m^3/h (Env) according to two models: dosimetric and epidemiological. HE Occ, HE Env correspond to dosimetric model and D Occ, D Env - to epidemiological one with the conversion conventions 1.425 for D Occ and 1.1 for D Env.

Place	Aerosol conditions	HE Occ [mSv/y]	HE Env [mSv/y]	D Occ [mSv/y]	D Env [mSv/y]	**HE Occ/ D Occ**	**HE Env/ D Env**
Attorney office	natural	1.46	0.76	0.87	0.68	**1.7**	**1.1**
	cigarette	2.70	1.45	2.00	1.55	**1.4**	**0.9**
UW Hoża pavilion	natural	0.08	0.04	0.06	0.04	**1.3**	**1.0**
	cigarette	0.25	0.15	0.31	0.24	**0.8**	**0.6**
CLOR bunker	natural	0.60	0.34	0.61	0.47	**1.0**	**0.7**
	cigarette	0.48	0.28	0.66	0.51	**0.7**	**0.5**
“Barbara”	natural	6.20	3.50	5.80	4.50	**1.1**	**0.8**
	natural	6.70	3.80	6.50	5.00	**1.0**	**0.8**

Fig. 2. RADEP DCF = f(Dp) for monodispersed particles

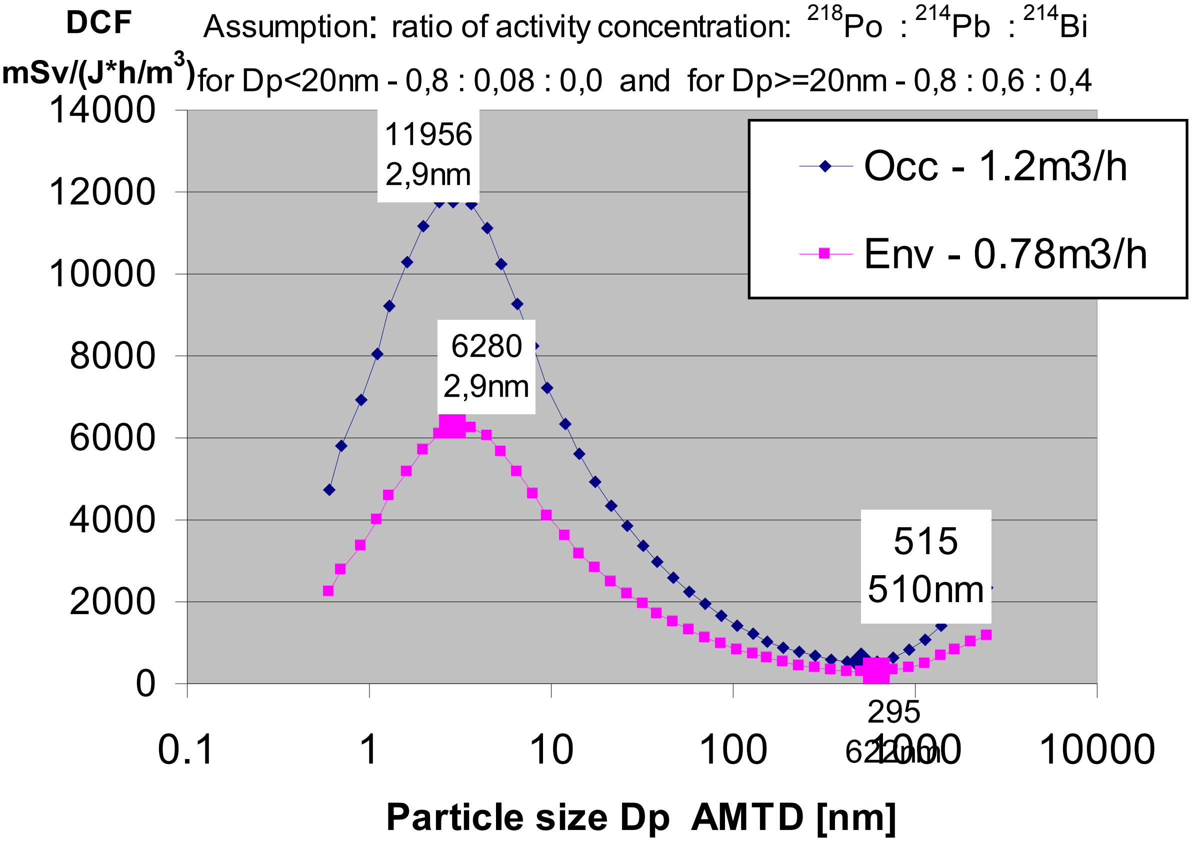

Fig. 3. The collection efficiency curves for all 8 stages

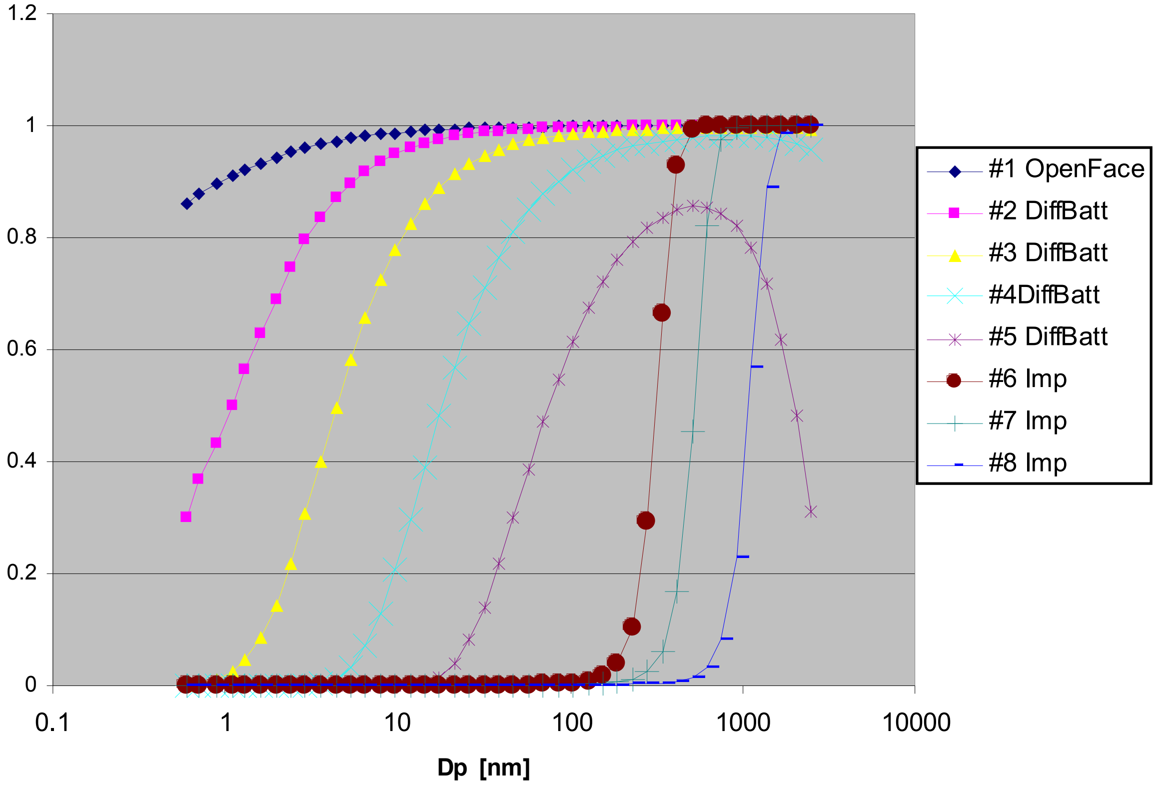

Fig. 4a. Particle size distributions

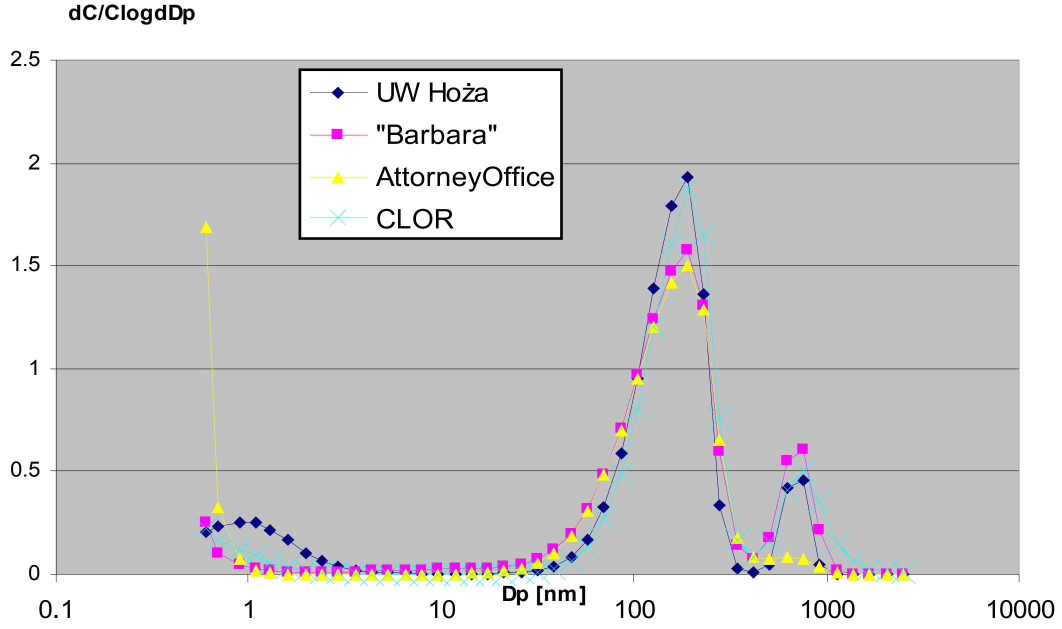

Fig. 4b. Particle size distributions

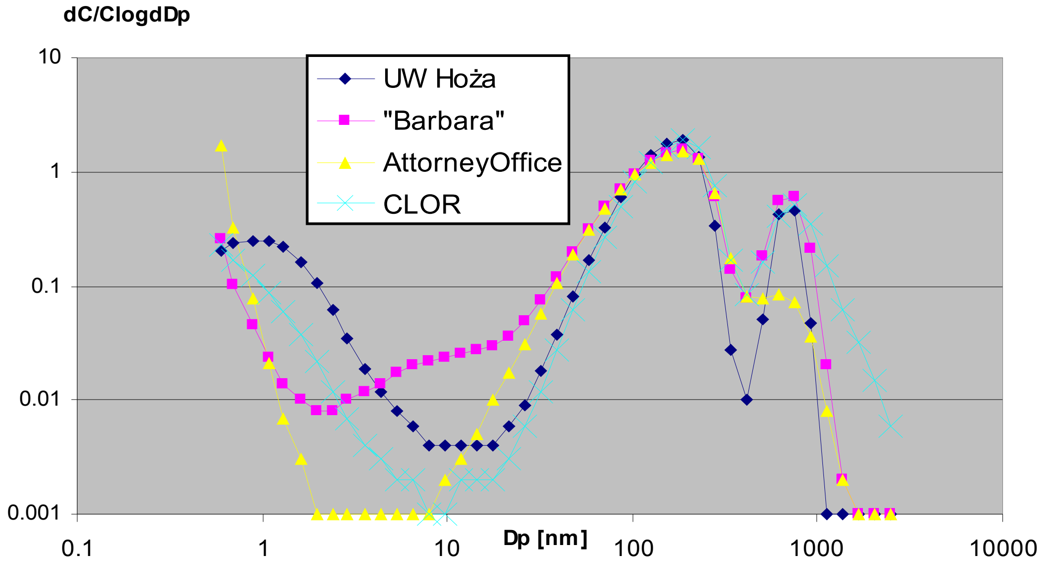

Fig. 1. Radon Progeny Particle Size Spectrometer (RPPSS)

THE INVENTORY AND RADIOLOGICAL IMPACT OF NATURALLY OCCURRING RADIONUCLIDES IN SOME ITALIAN NON-NUCLEAR INDUSTRIES

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ABSTRACT

The importance of NORM in Italy, from the radiation exposure point of view both for workers and for the public, is confirmed by a national decree (n. 241/2000), implementing the EU BSS, that provides the execution of controls for a set of work activities.

A project aimed at estimating environmental impact for some activities dealing with NORM is being carried out by the National Topic Centre on Physical Agents (CTN-AGF), coordination of Regional Environmental Protection Agencies (ARPA), which supports the National Agency for Environmental Protection and Technical Services (APAT) in collecting environmental information about physical pollutants (ionizing and non-ionizing radiations, noise). By now the following working categories have been chosen: phosphate and fertilizers industry, integrated steelworks, processing of zircon sands, oil and gas extraction, uranium mines, coal-fired power plants.

Radiological surveys have been carried out and technical data related to the various work activities have been collected by means of specific questionnaires sent to most of the involved factories: a centralized data base has been set up.

1. INTRODUCTION

A project aimed at estimating environmental impact of some activities dealing with NORM and coordinated by the Regional Environmental Protection Agencies (ARPA) is being carried out by the National Topic Centre on Physical Agents (CTN-AGF). The project is part of the research activities concerning the physical pollutants (ionizing and non-ionizing radiations, noise) launched by the National Agency for Environmental Protection and Technical Services (APAT) dealed with the following working categories, such as phosphate and fertilizers industry, integrated steelworks, processing of zircon sands, oil and gas extraction, uranium mines, coal-fired power plants.

The importance of NORM in Italy, from the radiation exposure point of view both for workers and for public, is confirmed by a national decree (No. 241/2000), implementing the EU BSS, that provides the execution of controls for a set of workink activities.

Information about presence and features of different working cycles has been obtained through field reports, representatives of sector associations or of the companies themselves.

Radiological surveys have been carried out to increase knowledge for some working activities as far as environmental impact is concerned on dusts, residues and products.

Technical data, related to the various working activities and sent by most of the involved factories, have been collected by means of specific questionnaires, and a centralized data base has been set up.

Preliminary results have been presented at Seventh International Symposium Natural Radiation Environment (NRE-VII), Rhodes, Greece, 20-24 May 2002 and the project has been exposed in this paper.

2. INDUSTRIAL ACTIVITY REVIEW

Table 10 – A synthesis of collected data about NORM involved industries.

SECTOR	WORKING ACTIVITY	N° OF COMPANIES or SITES NORM CONCERNED	ANNUAL TOTAL NATIONAL PRODUCTION or DIMENSION	NOTES	SOURCE
Processing of phosphate ores	Fertilizers industry	50 main companies	3.527.269 ton	Simple and complex mineral fertilizers	ISTAT, 2003 and Assofertilizzanti, 2002
	Phosphogypsum disposals	5 sites	From 200.000 to 6.000.000 m^3 each one	In two sites reclamation is concluded	Enichem, 2001

Processing of zircon sands	Tiles industry	50 main companies	600 million square metres	-	Assopiastrelle, 2004
	Refractories industry	9 companies	556.400 ton	-	
	Ceramic colourings and ceramic products industry	65 companies (potential)	-	In the manufacture of ceramic products direct use of zircon sands is not documented	Ceramicolor and Federceramica, 2002
Oil and gas extraction	Oil and gas extraction	ENI: about 7000 wells; EDISON: about 100 units	ENI gas extraction: $13{,}8\times10^9$ m^3 EDISON gas extraction: $1{,}4\times10^9$ m^3	Connate water (1.380.000 m^3/y), sludges ($\leq$ 2000 t/y) and productions tubings (15-20 per year) may have significant radioactivity levels (ENI)	ENI - AGIP Division and EDISON GAS, 2001
Coal-fired power plants	Coal-fired power plants	12 plants	Gross energy production: 31.000 GWh; coal consumption: 11 Mt	Individual and collective effective dose estimates are respectively: 0,42 µSv and 0,055 manSv.	ENEL Group, 2001
Steel production	Integrated steelworks	4 plants	26,7 million t	-	Federacciai, 2000
Processing of bauxite	Aluminium industry	1 company produces allumina and 1 company produces aluminium from allumina	1.020.000 t (allumina)	-	Assomet 2004 and personal communication from a company

3. DATA BASE OF NORM CONCERNED INDUSTRIES

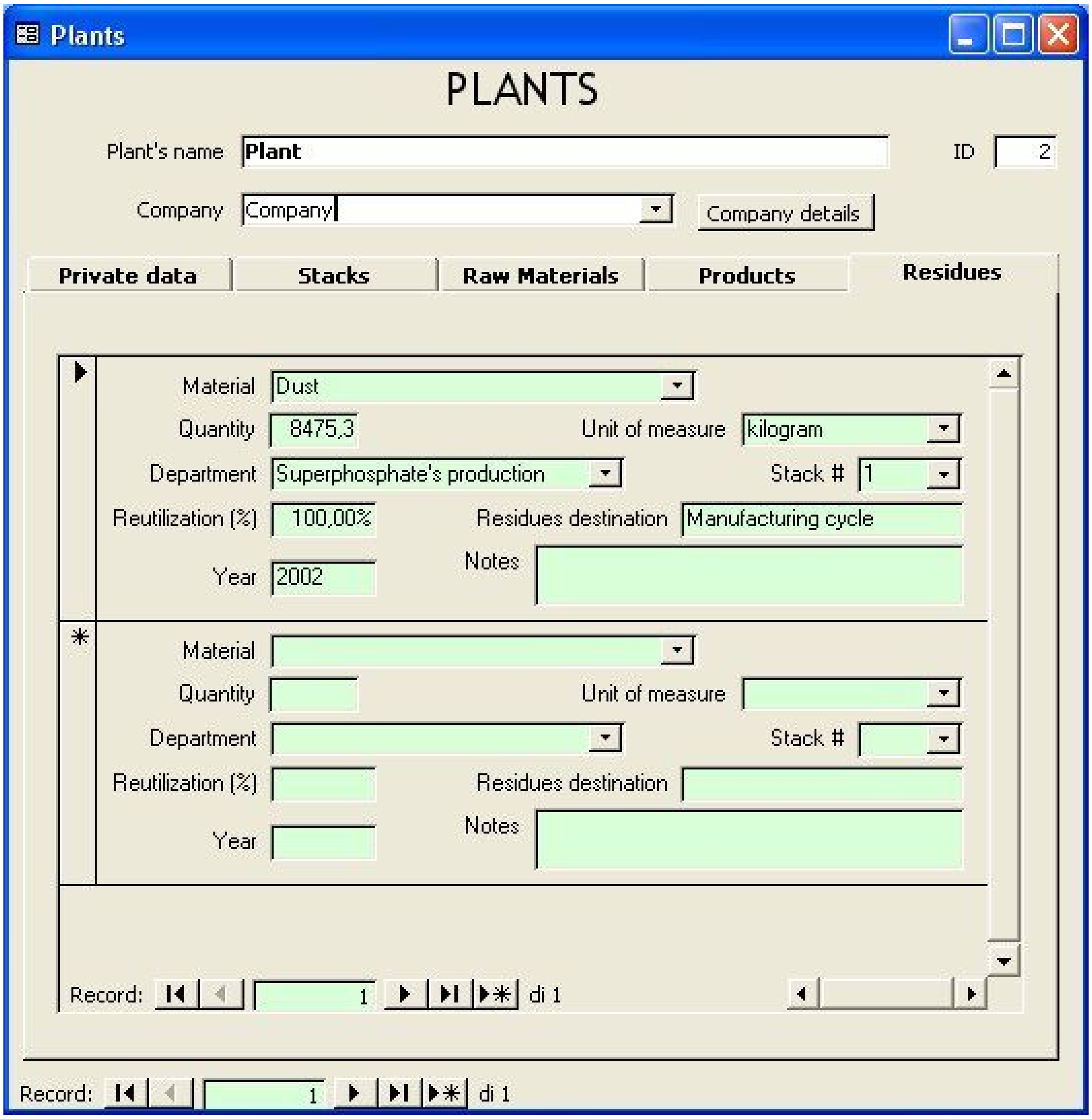
A data base of NORM concerned industries, containing adequate information in order to characterise environmental pressure of work related activities and to give input data for radiological impact estimates, has been set up.

This data base is composed of three sections:

- private data of companies and all its plants
- type, quantity and characteristics of raw materials (phosphate ores, zircon sands, bauxite...), products (fertilizers, refractory materials, aluminium...) and residues (dust, sludge and waste water) and technical data of the emissions (for instance: temperature, height and flow of chimneys)
- activity concentrations of ^{238}U chain, ^{232}Th chain and ^{40}K in materials (raw materials, products and residues) used or produced in working cycles of selected industries.

The data base is being compiled with data collected through questionnaires, that have been distributed to companies belonging to selected sectors, and through measurements results in specific samples.

Some data base input forms are shown in this paper.



PLANTS

Plant's name: Plant
ID: 2
Company: Company

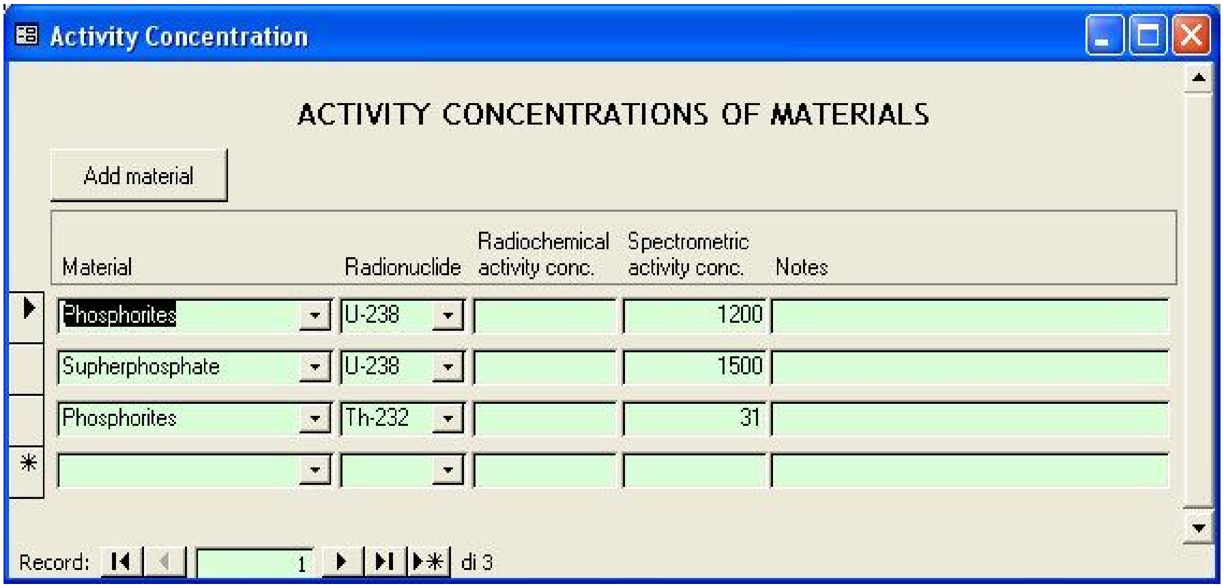
Material: Dust
Quantity: 8475,3
Unit of measure: kilogram
Department: Superphosphate's production
Stack #: 1
Reutilization (%): 100,00%
Residues destination: Manufacturing cycle
Year: 2002
Notes:

Material:
Quantity:
Unit of measure:
Department:
Stack #:
Reutilization (%):
Residues destination:
Year:
Notes:

Record: 1 di 1

Record: 1 di 1

Figure 1 – Input form for type, quantity and characteristics of residues



ACTIVITY CONCENTRATIONS OF MATERIALS

Material	Radionuclide	Radiochemical activity conc.	Spectrometric activity conc.	Notes
Phosphorites	U-238		1200	
Supherphosphate	U-238		1500	
Phosphorites	Th-232		31	

Record: 1 di 3

Figure 2 – Input form for activity concentrations of materials.

4. SECTORIAL RADIOLOGICAL STUDIES

4.1 Fertilizers industry

In Italy, on the bases of information provided by Assofertilizzanti (main fertilizers companies association), there are about 50 associated companies that produce complex, simple phosphate and simple potassic fertilizers, of which 17 are the main producers. Amongst them, three companies produce super phosphates by balanced reaction between phosphorites and sulphuric acid [1].

Additionally some new data is available about raw materials and products (the previous data have been presented by the same authors at the Seventh International Symposium Natural Radiation Environment (NRE-VII), Rhodes, Greece, 20-24 May 2002).

Table 11 – Activities concentrations (Bq/kg) in raw materials and products by ARPAV measurements (in brackets the percentage uncertainty at 68% confident level is given).

SAMPLES	^{238}U	^{226}Ra	^{232}Th	^{40}K	^{235}U
Moroccan MAP	2741 (15)	39 (6)	9 (7)	28 (6)	131 (5)
Russian MAP	41 (16)	1 (8)	14 (6)	37 (5)	2 (12)
Triple super phosphate	1506 (15)	352 (6)	7 (9)	92 (6)	69 (6)
Bony super phosphate	57 (18)	34 (6)	4 (7)	45 (6)	3 (21)

The breaking off of ^{238}U chain between ^{238}U and ^{226}Ra has been confirmed by Moroccan Monoammonium phosphate (MAP) and Triple super phosphate samples. The moderate ^{238}U content in Russian MAP may be due to phosphorites that are not used in its production.

For Bony super phosphate sample, the use of organic raw materials instead of conventional phosphate ores can explain moderate contamination of all natural radionuclides.

4.1.1 Estimate of collective effective dose by a simplified model

The collective effective dose on the Italian population due to the use of fertilizers in agriculture has been estimated by means of the simplified model given in UNSCEAR Report of 1982 ([2]: par. 64-65 Annex C, page 116).

This model, that takes into account both the introduction (ingestion of contaminated food and inhalation of resuspended material) and the external irradiation pathways, is the same used, for dose evaluations after deposition of nuclides emitted from a refractory plant, in the paper “A study concerning NORM in refractories industries” [3]. Only radionuclides of ^{238}U chain and ^{40}K have been considered, because the content of ^{232}Th and ^{235}U in fertilizers is not significant. The amount of radionuclides distributed in Italian soil has been derived from the quantities of national fertilizers consumption (ISTAT, 2003) and from average activity concentrations measured in various samples [3,4,5] as presented in Table 3.

Table 12 - Amounts of fertilizers used in Italy in year 2003 and average activity concentrations of ^{238}U chain nuclides and ^{40}K

Fertilizer	Used amount (t/y)	^{238}U (Bq/kg)	^{226}Ra (Bq/kg)	^{210}Pb (Bq/kg)	^{40}K (Bq/kg)	N. of samples averaged
Simple phosphatic	251.532	667	295	295		3
Simple potassic	152.336				14000	2
Complex phosphatic	1.385.070	262	107	157		15
Complex potassic	1.017.263				3379	15

In this study, it has been assumed, as far as inhalation and external irradiation pathways are concerned, that population stands on fertilized ground for the 1% of time.

Table 4 and Figure 3 show results of model estimates. The total committed collective effective dose is about 40 man·Sv/y; this is not a very high value and it can also be compared with the world wide estimate dose (UNSCEAR Report 1993) of 10000 man·Sv/y due to the use of fertilizers in agriculture. The crude estimate of the per caput dose, obtained by the ratio of the collective dose to the Italian population, is about 1 microSv/y, far below the action level of 300 microSv indicated by the Italian law [6].

Table 13 - Collective committed effective dose (manSv/y) due to national fertilizers consumption.

radionuclides	deposition			total
	ingestion	inhalation	external irradiation	
^{238}U	1,45E-01	1,22E-04	4,46E-01	2,56E-01
^{234}U	1,62E-01	1,51E-04		2,74E-01
^{230}Th	3,36E-01	2,78E-04		4,48E-01
^{226}Ra	1,95E+00	6,33E-05		2,06E+00
^{222}Rn		1,14E+00		1,14E+00
^{210}Pb	8,91E+00	1,27E-02		8,93E+00
^{210}Po	2,71E+01	3,82E-03		2,71E+01
^{40}K			5,78E-01	5,78E-01
total	3,86E+01	1,16E+00	1,02E+00	4,07E+01

From Table 4 and Figure 3 it is evident that the main contribution to dose comes from the ingestion pathway and that the most relevant nuclides are ^{210}Pb and ^{210}Po.

Caution is, here again, necessary in commenting this data due to the nature of the model (that ignores site specific data, single nuclide transfer coefficients, etc): an assessment with deterministic models, oriented particularly to analyse exposures of eventual critical groups, will have to be planned.

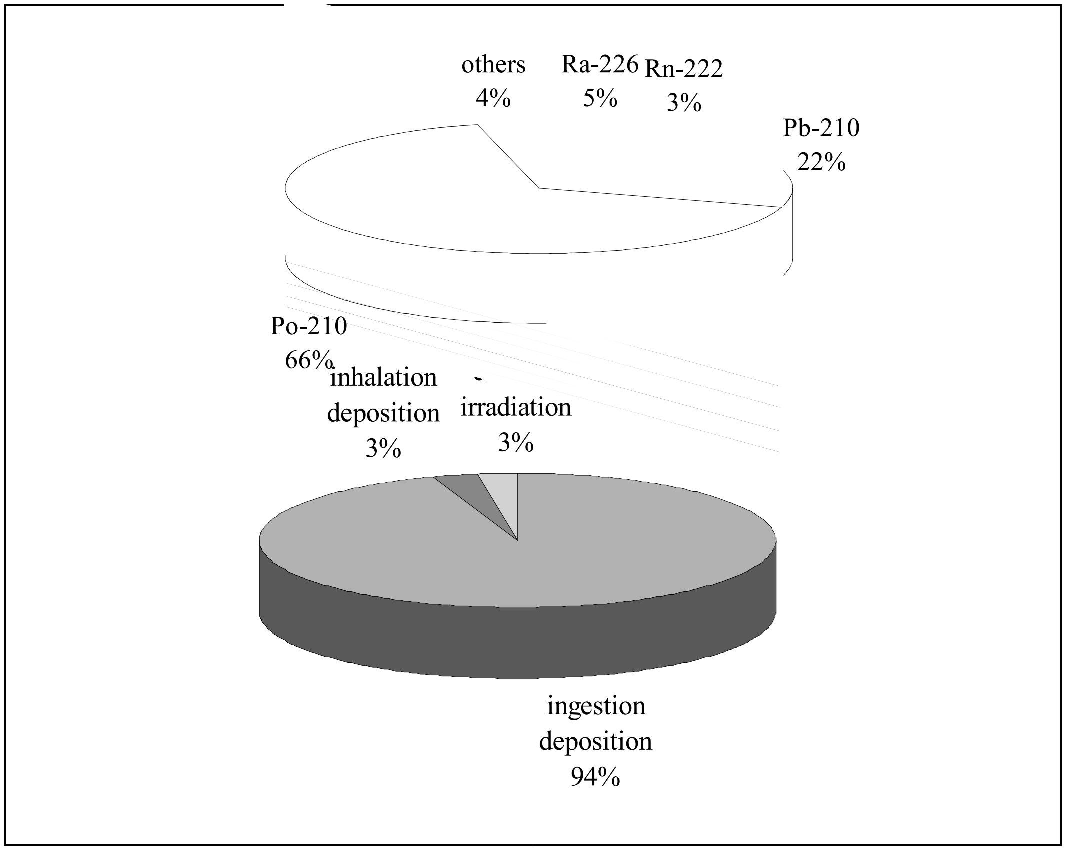


Figure 2 - Exposure radionuclides and pathway contributions.

4.2 Tile and refractory materials industry

The industrial production of tiles and refractory materials has been investigated by ARPAV because of its zircon sand or silicate contents, that may present elevated content of natural radionuclides [4].

The Italian ceramic tile industry enjoys an overall world leadership position, accounting for 43% of the tile production of the entire European Union and 13% of total world production. The industry comprises nearly 280 manufacturing facilities throughout Italy and has an output of more than 600 million square metres.

Assopiastrelle represents the main sector association with a 90% market representativity [7].

From Assopiastrelle data base, a set of 50 associated companies (70% market representativity) was selected and a simplified questionnaire was sent to them.

The questionnaire dealed with zircon sand or silicate used in the bulk of porcelain stoneware and in enamels preparation.

Only 32% of the interviewed companies have answered up to now and the results are shown in Table 5.

Table 14 – Quantity of zircon sand, silicate and enamels used by 32% of interviewed tiles industries in 2003.

	Zircon sands	Zircon silicates	Zircon sand/silicate based enamel preparation	Zircon sand/silicate based enamel purchase
amount (tons)	720	19.000	6.000-11.000	15.500

The Italian refractories industry is made up of 39 companies, 20 of which join the main sector association, Assopiastrelle (75% market representativity) [7].

Ten companies belonging to Assopiastrelle use zircon sands or semi-finished components zircon silicates based in the process, but only two of them use significative amounts of zircon sands (thousand of tons).

A study concerning NORM in refractories industries has been presented for this NORM IV Conference: this work shows the activity concentrations measurements by gamma spectrometry and radiochemical analysis, an estimate of collective effective dose by a simplified model and a national overlook [3].

4.3 Steelworks

Dust samples in thermal processes for a not-integrated steelwork have been collected. The samples have been analysed to assess their ^{210}Pb and ^{210}Po content through radiochemical analysis, in order to confirm the expected moderate contamination related to dusts coming from integrate steelworks.

Radiochemical analysis have been carried out in 2004 by University of Urbino and APAT and results are shown in Table 6.

The slight enrichment of ^{210}Pb and ^{210}Po in considered samples derives possibly from consumption of refractory materials in thermal process.

Table 15 – Activities concentrations (Bq/kg) in samples from a not-integrated steelwork; values represent the average of two laboratories analysis (University of Urbino and APAT); in brackets the percentage deviation of the two values from the average is given.

Samples	**^{210}Po**	**^{210}Pb**
converter electrofilter dust	422,0 (5,2)	360 (18,9)
blast fornace dust	58,7 (4,7)	50,2 (13,5)

4.4 Aluminium industry

Bauxite ores have moderate contents of natural radionuclides; following high temperature treatments, emissions may concentrate natural radionuclides, particularly ^{210}Pb and ^{210}Po [8].

At present, there are 50 allumina refineries in the world with a 55 Mtons/year production, 6 of which are in Europe with a 6,4 Mtons/year production.

In Italy the extraction of aluminium from bauxite is carried out by only one company and its production amounts to 1.020.000 tons/year.

The process is based on the digestion of bauxite with caustic soda at high temperature and pressure.

The alumina contained in the bauxite (about 50%) dissolves in the caustic phase and is separated; then the alumina is subsequently precipitated as hydrate and is sent to calcination where, at temperatures of about 1000°C the hydrate is transformed into product aluminium oxide (alumina) by elimination of the water of crystallization.

The other unextracted components represent the process residues (red mud), that are pumped to storage.

Some measurements in bauxite samples have been carried out by ARPAV. Table 7 presents the results, that confirm literature data [8] and shows radioactive levels more elevated than the average activities per unit mass in normal soil.

Table 16 - Activities concentrations (Bq/kg) in bauxite analysed by gamma spectrometry in ARPAV (percentage uncertainty at 95% confident level in brackets is given).

Samples	^{238}U	^{232}Th	^{40}K
Bauxite	333 (14)	383 (12)	35,5 (8,5)

REFERENCES

1. Assofertilizzanti, personal communication 2002
2. UNSCEAR, 1982, Sources and Effects of Ionising Radiation, United Nations, New York.
3. C. Zampieri et al., A study concerning NORM in refractories industries, NORM IV Conference – Szczyrk 2004, May 16th - 21 th
4. F. Trotti et al., Towards the identification of work activities involving NORM in Italy, Seventh International Symposium NATURAL RADIATION ENVIRONMENT (NRE-VII), Rhodes 2002, May 20th - 24 th.
5. L. Bruzzi, M.E. Canali, P. Lucialli, S. Righi, Misure di radioattività naturale e di radon in un impianto di produzione di fertilizzanti complessi. Atti del Convegno Nazionale “Problemi e tecniche di misura degli agenti fisici in campo ambientale”, 3-5 aprile 2001, Provana in Parella (TO).
6. D.Lgs. n° 241/00 “Attuazione della direttiva 96/29/EURATOM in materia di protezione sanitaria della popolazione e dei lavoratori contro i rischi derivanti dalle radiazioni ionizzanti”, Suppl. ord. G.U. n. 203 del 31/08/00.
7. Assopiastrelle, CerAnnuario, 2003-2004.
8. UNSCEAR, 1988, Sources, Effects and Risks of Ionizing Radiation, New York.

URANIUM ISOTOPES IN PUBLIC DRINKING WATER IN POLAND

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Abstract

^{238}U, ^{234}U and ^{235}U were determined in tap water from municipal water pipes supplied with water from rivers or lakes (surface water) and from wells (ground water), in various locations in Poland. Average activity concentrations of ^{238}U, ^{234}U and ^{235}U in tap water from surface waters were 9.94±7.22 mBq L^{-1}, 13.2±9.87 mBq L^{-1} and 0.43±0.31 mBq L^{-1}, respectively, whereas from ground water they were 4.53±6.00 mBq L^{-1}, 5.68±6.89 mBq L^{-1} and 0.18±0.27 mBq L^{-1}, respectively. Activity concentrations of ^{234}U were higher than ^{238}U. (^{234}U/^{238}U ratios ranged from 1.7 to 2.6), indicating the lack of equilibrium between these isotopes. The ^{234}U/^{238}U ratios for the surface and ground water were similar. Average ^{235}U/^{238}U ratio was 0.044±0.007 being close to 0.046 for natural uranium. Average annual intake with water and food was 7.48±3.96 Bq for ^{238}U and 9.45±0.46 Bq for ^{234}U. Annual committed effective

doses calculated from these intakes for adults were 0.34±0.18 μSv and 0.46±0.22 μSv, respectively.

Introduction

Uranium enters the human body mainly through ingestion, and to a considerably smaller degree by inhalation [1,2]. Contribution of drinking water in the total intake of uranium isotopes varies in wide ranges [3]. In the United States, the intake of water-derived uranium is at average 5 – 10 times greater than the food-derived uranium [4], though in New York City the contribution of water-derived uranium is much lower, being about 8% [2].

In Poland, the intake of uranium isotopes through ingestion was determined for the regions of central Poland [5], Wałbrzych [6] and the Świetokrzyskie Mountain [7]. It was found that in these regions the contribution of water-derived ^{238}U and ^{234}U was from about 66% to 91%, and from 76% to 93%, respectively.

The aim of the present work was to determine activity concentration of uranium isotopes in tap water in various sites in Poland. Total ingestion of ^{238}U and ^{234}U was calculated using the data for drinking water obtained in this work, and data for the intake with foodstuffs from the publications [5,6,7].

Materials and methods

Samples of tap water were collected in years 2002 and 2003 from water supply systems located in various parts of Poland. The systems were supplied with surface water from rivers or lakes (15 water pipes) and from deep underground wells (16 water pipes). The sites of tap water collection are presented in Fig.1.

Determinations of uranium isotopes were performed in 5-l. samples of water. ^{232}U was used as an internal tracer for counting alpha activity and chemical recovery. After evaporation of water, uranium was chemically separated by anion exchange and extraction. Finally, uranium was electrodeposited on a stainless steel disc. Activity of deposited uranium was measured with alpha spectrometry system. PIPS detectors for alpha spectrometry were placed in vacuum chamber and connected with multichannel analyzer Multiport II MCA (Canberra MP2-GE) with GENIE 2000 spectroscopy software. Details of the analytical procedure were described elsewhere [6].

Average uranium tracer recovery was approx. 77%, lower limit of detection (LLD) with the counting time of 82.000 s was 0.22 mBq/sample for ^{234}U and 0.29 mBq/sample for ^{238}U and ^{235}U.

Results

Activity concentrations of ^{238}U, ^{234}U and ^{235}U in drinking water supplied from surface water are presented in Table 1. Activity concentration of ^{238}U ranged from 1.79±0.21 mBq L^{-1} in Kraków up to 23.9±1.66 mBq L^{-1} in Legnica, whereas concentrations of ^{234}U ranged from 2.47±0.27 mBq L^{-1} in Bydgoszcz to 34.1±2.33 mBq L^{-1} in Legnica. Concentration of ^{235}U were the lowest in Kraków (0.10±0.04 mBq L^{-1}) and the highest in tap water collected in Wrocław from water pipe supplied from Oława river 19.9±1.36 mBq L^{-1}. Mean activity concentrations of ^{238}U, ^{234}U and ^{235}U were 9.94 ±7.22 mBq L^{-1}, 13.2±9.87 mBq L^{-1} and 0.43±0.31 mBq L^{-1}, respectively. In all samples the activity concentration of ^{234}U was higher

than that of ^{238}U. The activity concentration ratio was in the range from 1.07 to 2.60, with mean value 1.34±0.32.

Fig.1. Sites of collection of tap water supplied from: ● surface water, ▲ ground water, ♦ surface and ground water

Activity concentrations of ^{238}U, ^{234}U and ^{235}U in drinking water supplied from ground water are given in Table 2. In the majority of tap waters the activity concentrations of uranium isotopes were much lower than those supplied from surface water. The lowest concentration of ^{238}U was found in Ostrołęka and Gubin (0.36 mBq L^{-1}) and the highest in Suwałki (23.2±1.34 mBq L^{-1}). Similarly as in the case of tap water supplied from surface water, the activity concentration of ^{234}U were higher than those of ^{238}U, they ranged from 0.46 ±0.09 mBq L^{-1} in Ostrołęka up to 25.7 ±1.48 mBq L^{-1} in Suwałki. In six out of 16 water pipes the concentrations of ^{235}U were below the lower limit of detection (0.06 mBq L^{-1}); the highest value was noted in Suwałki (1.04 ±0.04

mBq L^{-1}). Mean activity concentrations of ^{238}U, ^{234}U and ^{235}U were 4.53 ±6.00 mBq L^{-1}, 5.68±6.89 mBq L^{-1} and 0.18±0.27 mBq L^{-1}, respectively. For the calculation of the mean value of ^{235}U it was assumed that in the samples with the concentration of this radionuclide below LLD, its concentration was 0.5 LLD, i.e. 0.03 mBq L^{-1}.

Table 1. Activity concentrations of ^{238}U, ^{234}U and ^{235}U, and ^{234}U/^{238}U ratio in drinking water supplied from surface water

Location	River or lake	^{238}U mBq L^{-1}	^{234}U mBq L^{-1}	^{235}U mBq L^{-1}	^{234}U/^{238}U ratio
Szczecin	Miedwie lake	14.5±0.93[a)]	15.5±1.02	0.56±0.07	1.07
Białystok	Supraśl river	6.91±0.58	8.35±0.69	0.29±0.07	1.21
Bydgoszcz	Brda river	2.00±0.23	2.47±0.27	0.11±0.04	1.24
Płock	Vistula river & ground water[b)]	4.56±0.40	5.87±0.50	0.19±0.05	1.29
Poznań	Warta river	13.6±0.93	16.11±1.09	0.48±0.08	1.19
Warszawa	Zegrzyn lake	6.43±0.81	7.86±0.99	0.28±0.08	1.22
Łódź	Pilica river Tomaszów[c)]	2.59±0.23	3.32±0.23	0.15±0.04	1.28
Legnica	Kaczawa river (infiltration)	23.9±1.66	34.1±2.33	0.96±0.09	1.43
Wrocław	Oława river (infiltration)	19.9±1.36	26.4±1.78	0.98±0.12	1.32
Wrocław	Nyska Kłodzka river	10.9±0.59	13.5±0.73	0.48±0.05	1.24
Wałbrzych	Bóbr river (infiltration)	5.07±0.42	13.2±0.98	0.24±0.08	2.60
Zamość	Łabuńka river (infiltration)	20.7±1.34	29.4±1.88	0.90±0.11	1.42
Kraków	Raba river	1.79±0.21	2.97±0.30	0.10±0.04	1.66
Rzeszów	Wisłok river Zwięczyca[c)]	11.4±0.81	13.5±0.95	0.52±0.07	1.18
Krosno	Wisłok river Iskrzynia[c)]	4.85±0.39	5.94±0.46	0.14±0.04	1.22
Mean ±SD		9.94±7.22	13.2±9.87	0.43±0.31	1.37±0.37

[a] Value ± counting error at the 95% confidence level.

[b] 1:1 mixture

[c] Site of the water intake

The assessment of uranium intakes with food and water performed in three regions of Poland showed that the variability of food-derived activity of ^{238}U and ^{234}U was smaller than that of water-derived activity [5-7]; respective values from these works are summarised in Table 3. In these regions the annual intakes of ^{238}U ranged from 8.08 Bq to 22.2 Bq with an average 12.8±8.14 Bq, whereas the annual intake of ^{234}U was from 9.69 Bq to 31.8 Bq with an average 18.7±11.6 Bq. The activity of ^{238}U and ^{234}U which enters human beings with ingested food was at average equal to 2.27±0.46 Bq and 2.66±0.74 Bq, respectively. These values were obtained for the regions with a wide variety of natural radionuclides [8], hence it can be supposed that they may also represent other regions of Poland. Therefore, in the present work it has been assumed that food-derived intakes in the sites studied are equal to the average food-derived intakes given in Table 3. Annual intakes of ^{238}U and ^{234}U with water were evaluated from the concentrations of these radionuclides in tap water (Tables 1 and 2);

Table 2. Activity concentrations of ^{238}U, ^{234}U and ^{235}U, and ^{234}U/^{238}U ratio in drinking water supplied from ground water

Location	^{238}U mBq L^{-1}	^{234}U mBq L^{-1}	^{235}U mBq L^{-1}	^{234}U/^{238}U ratio
Słupsk	10.5±0.73[a]	12.3±0.84	0.58±0.08	1.17
Koszalin	0.80±0.07	1.36±0.11	<0.06	1.70
Elbląg	2.07±0.15	2.44±0.17	0.09±0.02	1.18
Suwałki	23.2±1.34	25.7±1.48	1.04±0.04	1.11
Olecko	1.90±0.22	2.92±0.30	0.10±0.04	1.54
Ełk	10.3±0.86	12.2±1.00	0.40±0.08	1.18
Olsztyn	4.71±0.41	5.76±0.48	0.12±0.04	1.22
Ostrołęka	0.36±0.08	0.46±0.09	<0.06	1.28

Toruń	6.90±0.55	8.63±0.67	0.28±0.06	1.25
Włocławek	0.89±0.12	0.99±0.13	<0.06	1.11
Łódź	1.34±0.11	1.56±0.13	0.06±0.02	1.16
Gubin	0.36±0.06	0.52±0.07	<0.06	1.44
Kalisz	0.61±0.06	0.67±0.07	<0.06	1.10
Lublin	2.07±0.18	2.28±0.19	0.08±0.03	1.10
Opole	5.19±0.41	11.4±0.82	0.16±0.04	2.19
Tarnobrzeg	1.35±0.11	1.63±0.12	<0.06	1.21
Mean ± SD	4.53±6.00	5.68±6.89	0.18±0.27b)	1.31±0.29

a) Value ± counting error at the 95% confidence level.

b) In the calculation it was assumed that in the samples with concentration of ^{235}U below LLD, the concentration was 0.5 LLD.

Annual consumption of water for adults was taken as 730 l after Guidelines for drinking water quality [9]. Intakes with food were assumed to be 2.27±0.46 Bq and 2.66±0.74 Bq for ^{238}U and ^{234}U, respectively. The estimated total intakes with water and food are given in Table 4.

The total intakes varied in wide ranges; they were from 2.54 Bq to 19.7 Bq for ^{238}U and from 2.99 Bq to 27.6 Bq for ^{234}U. Contribution from water were similar for both of radionuclides ranging from about 10% to about 90%.

Annual committed effective doses resulting from 1-year ingestion were calculated from the annual intake of ^{238}U and ^{234}U (Table 4) and from the dose coefficients given by the International Commission on Radiological Protection [10]. Table 5 gives values calculated for the average intake and for locations supplied with surface and ground water. Average annual intakes for inhabitants of all studied locations were 7.48±3.96 Bq for ^{238}U and 9.45±0.46 Bq for ^{234}U; respective doses were 0.34±0.18 μSv and 0.46±0.22 μSv, being in total 0.8 μSv.

Table 3. Annual intakes of ^{238}U and ^{234}U with food and water and contribution of food-derived isotopes, Bq [5–7]

Region	^{238}U Total	^{238}U Food-derived	^{234}U Total	^{234}U Food-derived
Central Poland	8.08±1.57	2.01±0.19	9.69±1.56	2.24±0.18
Wałbrzych	8.13±0.38	2.81±0.20	14.5±0.70	3.52±0.24
Świętokrzyskie Mountain	22.2±0.97	2.00±0.17	31.8±1.48	2.21±0.20
Average ± SD	12.8±8.14	2.27±0.46	18.7±11.6	2.66±0.74

Discussion

The results of this work show that activity concentrations of uranium isotopes in tap water in various locations in Poland can vary within wide ranges. Tap water supplied from ground waters contain ^{238}U in concentrations from 0.36 Bq L^{-1} to 23.2 Bq L^{-1} and ^{234}U in concentrations from 0.52 mBq L^{-1} to27.7 mBq L^{-1}. Tap water supply from surface waters contain ^{238}U in concentrations from 1.79 Bq L^{-1} to 23.9 Bq L^{-1} and ^{234}U in concentrations from 2.47 mBq L^{-1} to 34.1 mBq L^{-1}. Within these ranges are also the activity concentrations reported by Skwarzec et al. [11] for the Gdańsk agglomeration. The lowest concentrations measured in the present study were almost the same as those given in [12] for the USA. However, the highest concentrations in Poland were about 1/3 of those in the USA (77 mBq

Location	^{238}U		^{234}U	
	Bq	%	Bq	%
Szczecin	12.9±0.82	82.3	14.0±1.05	81.0
Białystok	7.32±0.63	68.9	8.75±0.90	70.0
Bydgoszcz	3.73±0.49	39.1	4.46±0.77	40.5
Płock	5.60±0.55	59.4	6.94±0.83	61.7
Poznań	12.2±0.82	81.4	14.4±2.09	81.6
Warszawa	6.97±0.75	67.4	8.39±1.09	68.4
Łódź[a)]	3.65±0.48	37.7	4.44±0.76	40.3
Legnica	19.7±1.30	88.5	27.6±1.86	90.4
Wrocław	16.8±1.09	86.5	21.9±1.50	87.9
Wrocław	10.2±0.63	77.8	12.5±0.92	78.8
Wałbrzych	5.97±0.56	61.9	12.3±1.03	78.4
Zamość	17.4±1.08	86.9	24.1±1.56	89.0
Kraków	3.58±0.49	36.5	4.82±0.78	45.0
Rzeszów	10.6±0.75	78.6	12.5±1.02	78.8
Krosno	5.81±0.55	60.9	6.99±0.82	62.0
Słupsk	9.94±0.71	77.1	11.6±0.97	77.2
Koszalin	2.86±0.47	20.4	3.65±0.75	27.2
Elbląg	3.78±0.48	39.9	4.44±0.76	40.2
Suwałki	19.2±1.08	88.2	21.4±1.31	87.6
Olecko	3.66±0.49	37.9	4.79±0.78	44.5
Ełk	9.79±0.78	76.8	11.6±1.04	77.0
Olsztyn	5.71±0.55	60.2	6.86±0.83	61.3
Ostrołęka	2.54±0.47	10.4	2.99±0.75	11.2
Toruń	7.31±0.61	68.9	8.95±0.89	70.4
Włocławek	2.92±0.47	22.2	3.38±0.75	21.4
Gubin	2.54±0.48	10.4	3.03±0.75	12.5
Kalisz	2.72±0.47	16.4	3.14±0.75	15.6
Lublin	3.78±0.48	39.9	4.32±0.76	38.5
Opole	6.06±0.55	62.5	11.0±0.96	75.8
Tarnobrzeg	3.26±0.47	30.2	3.84±0.75	30.9

Table 4. Annual intakes of ^{238}U and ^{234}U from drinking water and food (Bq) and contribution of water-derived uranium (%)

[a)] Calculated for mixed water used for consumption by the Łódź inhabitants.

L^{-1} for ^{238}U and 117 mBq L^{-1} for ^{234}U. Concentrations similar to those in Poland were found for New York City tap water (^{238}U: 0.87 ± 0.18 mBq L^{-1}, ^{234}U: 1.04 ± 0.19 mBq L^{-1}) [2] and in Salt Lake City (^{238}U: 17.8 ±3.33 mBq L^{-1}, ^{234}U: 29.6 ±3.70 mBq L^{-1}) [13]. Despite the variations observed in the present work, activity concentrations for ground water are at average lower than those for surface water. This is in contrast to the situation in the USA, where concentrations in ground waters were in some states up to 4 times higher than in surface water. However, in many states the uranium concentrations in tap water taken from ground and surface water were identical [4]. This variability of uranium concentrations is understandable, because uranium concentration in water depends on many factors, such as the uranium concentration in the aquifer rock and chemical composition of water, including pH, redox potential, content of oxygen, CO_2, and complexing agents [4,12].

Table 5. Annual intake of ^{238}U and ^{234}U with food and water by adult population in locations supplied with surface water (SA) and ground water (GW), and associated collective effective doses

	^{238}U$^{*)}$ Intake, Bq	Dose, µSv	^{234}U$^{*)}$ Intake, Bq	Dose, µSv
Average, for all locations	7.48±3.96	0.34±0.18	9.45±0.46	0.46±0.22
Locations supplied with SW	9.49±5.37	0.43±0.24	12.3±7.28	0.60±0.36
Locations supplied with GW	5.58±4.38	0.24±0.20	6.80±5.03	0.32±0.25

*) Dose coefficient (µSv Bq^{-1}): 0.045 for ^{238}U and 0.049 for ^{234}U [10]

In all analyzed samples of water the activity concentration of ^{234}U was higher than that of ^{238}U. The activity ratio of ^{234}U/^{238}U were similar for tap water supplied from ground and surface waters being at average 1.31±0.29 and 1.37±0.37, respectively (Table 1 and 2). Numerous studies on ^{238}U and ^{234}U in water indicate that these isotopes occur in disequilibrium state and that with a few exceptions, waters contain more ^{234}U than ^{238}U [4,11, 12,14,15,16]. Higher activity of ^{234}U in waters results from the ^{234}U atom displacement from crystal lattice of uranium minerals. ^{234}U atom is liable to be oxidized to the hexavalent stage and can be leached into the water phase more easily than its parent nuclide ^{238}U [1].

The average activity ratio of ^{235}U to ^{238}U for water samples was equal to 0.044±0.007 which is very close to the value 0.046 for natural uranium.

Annual committed effective dose from intake of ^{238}U and ^{234}U was 0.80±0.28 μSv. In locations where tap water was taken from surface water this dose was about 1 μSv, whereas in locations in which tap water was taken from surface water the dose was lower, being 0.56 μSv. Dose from uranium isotopes constitutes only a small fraction of the dose from natural radionuclides of uranium and thorium series ingested with food and water which was estimated to be about 90 μSv [17].

References

[1] United Nations Scientific Committee on the Effects of Atomic Radiation. Sources and effects of ionizing radiation, Report to the General Assembly. New York: United Nations, 1977

[2] I.M.Fisenne, P.M. Perry, K.M.Decker, H.W.Keller,. The daily intake of ^{234,235,238}U, ^{228,230,232}Th and ^{226,228}Ra by New York City residents. Health Phys., 1994, 67:115-121

[3] United Nations Scientific Committee on the Effects of Atomic Radiation. Sources and effects of ionizing radiation, Report to the General Assembly. New York: United Nations, 1988

[4] C.T.Hess, J.Michel, T.R.Horton , H.M.Prichard, W.A.Coniglio, The occurrence of radioactivity in Public water supplies in the United States. Health Phys., 1985, 48: 553-586

[5] Z.Pietrzak-Flis, L.Rosiak, M.M.Suplińska, E.Chrzanowski, S.Dembińska, Daily intakes of ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th and ^{226}Ra in adult population of central Poland. Sci. Total Environ., 2001,273: 163-169

[6] Z.Pietrzak-Flis, M.M.Suplińska, L.Rosiak, The dietary intake of ^{238}U, ^{234}U, ^{230}Th, ^{232}Th, ^{228}Th, and ^{226}Ra from food and drinking water by inhabitants of Walbrzych region, J. Radioanal. Nucl. Chem., 1997, 222: 189 –193

[7] Z.Pietrzak-Flis, L.Rosiak, E.Chrzanowski, S.Dembińska, The daily intake of ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th and ^{226}Ra by adult inhabitants of Świętokrzyskie Mountains area, Annual Report 1998 – 1999, Central Laboratory for Radiological Protection, Warsaw 2000, p. 60 –62

[8] M.Biernacka, W. Bekiert, A.Koczyński, A.Sosińska, Monitoring of Radioactive Contamination, Warsaw, CLOR, 2002 (in Polish)

[9] Guidelines for drinking-water quality, Second Edition, Vol.1, Recommendations, WHO, Geneva, 1993

[10] International Commission on Radiological Protection, Age-dependent doses to members of the public from intake of radionuclides: part 5. Compilation of ingestion and inhalation dose coefficient. Ann ICRP 1996:26(1). ICRP Publication 72, Pergamon Press, Oxford

[11] B.Skwarzec, D.I.Strumińska, A.Borylo, The radionuclides ^{234}U, ^{238}U and ^{210}Po in drinking water in Gdańsk agglomeration (Poland), J.Radioanal. Nucl. Chem., 2001,250: 315 –318

[12] C.R.Cothern, W.L. Lappenbusch, Occurrence of uranium in drinking water in the U.S., Health Phys., 1983, 45:89-99

[13] N.P.Singh, D.P.Burleigh, H.M.Ruth, McD.E.Wrenn, Daily U intakes in Utah residents from food and drinking water, Health Phys., 1990, 59:333-337

[14] Z.Pietrzak-Flis, I.Kamińska, E.Chrzanowski, Uranium isotopes in waters and bottom sediments of rivers and lakes in Poland, submitted for publication in Nukleonika

[15] A.J.Plater, M. Ivanovich, R.E.Dugdale, Uranium series disequilibrium in river sediments and waters: the significance of anomalous activity ratios. Appl. Geochem., 1992, 7: 101-110

[16] R.L.Fleischer, Isotopic disequilibrium of uranium: alpha-recoil damage and preferential solution effects, 1980, Science 207: 979-981

[17] Z.Pierzak-Flis, Natural radionuclides in food of Polish population, Postępy Techniki Jądrowej, 1999, 42: 18-26 (in Polish)

CHARACTERISATION OF SCALE FROM A FORMER PHOSPHORIC ACID PROCESSING PLANT

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ABSTRACT

A wide variety of industries extract and/or process ores and minerals containing naturally occurring radioactive material (NORM). In many cases the industrial processing of natural feedstock results in radioactive material becoming concentrated in (by-) products, wastes and plant installations. The main sources of NORM are members of the ^{238}U and ^{232}Th decay chains. The radioelements of greatest concern are radium, lead and polonium, due to their radiological and toxicological properties when inhaled and/or ingested.

Scale samples were collected from a phosphoric acid processing plant, which is currently in the process of being demolished. These materials were analysed to determine the nature and concentration of naturally occurring radioactive material (NORM) retained in pipe work and process plant. Three areas of the site were investigated; 1) the ‘Green Acid Plant’, where crude acid was concentrated; 2) the green acid storage tanks; and 3) the Purified White Acid (PWA) plant, where inorganic impurities were removed. The scale samples predominantly comprise: fluorides (*e.g.* malladrite, iron oxide fluoride); calcium sulphate (*e.g.* bassanite); and an assemblage of mixed fluorides and phosphates (*e.g.* iron fluoride hydrate, calcium phosphate) respectively, which can be related to the process occurring at each of these locations. The radioactive inventory is dominated by ^{238}U and its decay chain products and significant fractionation along the series occurs. Compared to the feedstock ore, elevated concentrations (≤ 8.8 Bq/g) of ^{238}U, in equilibrium with its daughter ^{234}Pa, were found in installations where the process stream was rich in fluorides and phosphates. Enriched levels (≤ 11 Bq/g) of ^{226}Ra were found in association with precipitates of calcium sulphate. ^{210}Pb levels in excess of its parent ^{226}Ra were also noted in many materials from the PWA plant, which may be attributed to the purification process in this installation.

Keywords: NORM, industry, radioactivity, phosphate rock, uranium decay chain

1. INTRODUCTION

Enhanced concentrations of naturally occurring radioactive material (NORM) arise in industry where radioisotopes become mobile and subsequently accumulate in (by-) products, wastes and plant installations [1]. The main sources of NORM are from parent actinides ^{238}U and ^{232}Th, which decay to stable lead, through a series of intermediate radioactive daughters [2]. The daughters of greatest radiological concern are ^{226}Ra, ^{228}Ra, ^{222}Rn, ^{210}Pb and ^{210}Po, due to their radiological properties and potential to invade the human environment, by inhalation and/or ingestion, thereby becoming a health hazard [3]. It is, therefore, necessary for this radioactive material to be disposed of responsibly so that it remains sufficiently isolated from the human environment [4].

The need to dispose of diffuse NORM waste will have environmental and regulatory implications that so far have not been fully appreciated [5]. For example, contaminated installations require disposal, or decontamination and disposal of the resultant waste. Both options are accompanied by loss of production and considerable costs are incurred. In addition, by-products and waste streams are produced in large volumes and are frequently dumped on site, or go to landfill. Furthermore, in many cases the wastes were produced a long time ago, and were disposed of as non-radioactive materials, thereby occupying valuable land needed for construction and /or agriculture. At the root of the problem is a lack of understanding of: 1) The extent of NORM contaminated land; 2) the concentration of the NORM in these industrial sites; and 3) the quantity of the NORM to be disposed of under the current directives.

In order to investigate the extent of radionuclide contaminated land, a database of U.K. sites contaminated by NORM was compiled. Sites were characterised according to the nature of the industry, the radionuclides present, the aerial extent of the contamination, and whether the site is under institutional control. In addition, information was gathered on the nature of the hazard *i.e.* whether the radioactivity is in installations, buried, in (by) products etc. (Table 1). From this database a phosphoric acid processing works was selected in order to investigate the extent and nature of radionuclide contamination.

2. THE PHOSPHATE INDUSTRY

Background. A phosphate processing plant on the North West coast of England has produced phosphoric acid since 1954. The company imported phosphate ore, of a sedimentary origin, containing approximately 1490 Bq/kg (120 ppm) uranium, from Morocco and Israel until mid-1992 [6]. This ore was reacted with sulphuric acid to produce a ‘green acid’, using the Norsk Hydro hemidihydrate wet phosphoric acid production process and was then further purified to produce food, technical and salts grade phosphoric acid. The waste product from this process was phosphogypsum slurry, the insoluble fraction resulting from the initial digestion of the ore with the sulphuric acid, and an acid waste stream resulting from further processing of the ‘green acid’. The combined wastes were discharged under UK authorisation, into the sea [6].

In 1992, however, the company significantly modified its manufacturing procedure. Two main changes in operations occurred: 1) The on-site manufacture of phosphoric acid from phosphate ore was abandoned, and instead crude phosphoric acid, ‘green acid’, (with a uranium activity of 744 Bq/kg) was imported from Morocco and Mexico, and purified at the works; and 2) the introduction of a treatment plant, which treated the liquid raffinate waste with quick lime (CaO) to produce a solid comprising calcium sulphate and calcium hydroxyapatite [7]. The calcium hydroxyapatite has a crystal structure similar to that of natural phosphate rock in which the heavy metals are “locked into” the insoluble lattice. The uranium, along with other metals, primarily cadmium [8], is said to be permanently encapsulated within the solid, called Ufex, which was landfilled on site. Consequently discharge to sea ceased.

Current status. The phosphoric acid processing plant ceased to be operational in 2002. Installations from the phosphoric acid purification process are currently being demolished and this is due to be completed by mid-2004.

The company is working with the regulator on a remediation plan for the site. The Ufex will remain on site in engineered clay-lined landfills, which are capped with a waterproof membrane and a metre of soil. Leachate, from the Ufex cells, is monitored by the regulator twice a year under its radioactive monitoring programme, and the results published in an annual report [9]. The leachate is discharged via the former phosphogypsum waste pipe into the sea. The radioactive discharge authorisation is still extant.

Aims and Objectives. It has long been known that in the process of phosphoric acid production, radionuclides in the uranium decay chain become partitioned into products and by-products (see [10] and [11]). However, in a study conducted in 1992 at the UK chemical works it was suggested that a proportion of the radionuclides were retained on site in the pipe work and process plant [6]. Should this be the case, the industry would be faced with decontamination/disposal issues when maintaining or demolishing processing plant.

Thus, the aim of this study was to characterise scale, from selected stages of the processing stream, in terms of mineralogy and radioactivity. The overall objectives of this characterisation programme were to: 1) Establish the process areas, if any, which accumulate radioactivity and the fractionation that had occurred along the natural decay series chains; and 2) quantify the form and nature of the material that was being disposed.

3. SOURCES OF CONTAMINATION

Areas Investigated. Widespread scaling of the process plant and storage tanks was observed, however, due to the on-going demolition works samples were taken from only a limited number of areas. These areas were as follows:

1. The Green Acid Plant; where the acid was concentrated by vacuum evaporation with forced circulation. The plant was utilised both pre- and post-1992 for concentrating the acid. Two scale samples were taken from a pipe that linked the concentrator with the ejector, which was used to pull the vacuum. This was positioned at the top of the building, but has since been dismantled.

2. The green acid storage tanks; used in both processes for storing concentrated phosphoric acid from the Green Acid Plant, and for pre-concentrated acid from Morocco/Mexico. The tanks were installed with agitators to keep the solids in suspension. A scale sample was taken from one of the agitators and also from the inside of one of the tanks.

3. The Purified White Acid (PWA) Plant; where inorganic impurities are removed by means of an extraction process in which pre-purified acid was contacted with a solvent (methylisobutyl ketone) in several stages. Together with small amounts of impurities, the phosphoric acid was

transferred to the organic phase, while most of the impurities remained in the aqueous phase. In order to achieve a higher yield of P_2O_5, the underflow from the solvent reaction vessel was transferred to a second extraction column, and reacted with sulphuric acid so that the cationic impurities remained in the aqueous phase as sulphates [14]. This waste stream then went to the raffinate treatment plant prior to landfill. The purified acid from both columns underwent further processing in additional plant installations to remove arsenic and fluorine, thereby producing a food grade phosphoric acid. Six samples were taken from the PWA plant at various locations as illustrated in Figure 2.

4. MINERALOGY

All samples were prepared for analysis by drying in an oven at 70ºC for 24 hours. The samples were then ground, using a Tema disc mill, to a fine powder (~ 5 µm) as required for x-ray analysis. A certified standard of igneous phosphate rock, from South Africa, was also analysed in order to determine the precision and accuracy in the sample data (Table 2). The mineralogy of the samples was obtained by x-ray diffraction (XRD) analysis and are summarised in Table 3.

A sub-set of samples were also examined by Scanning Electron Microscope (SEM). A JOEL JXA840 was used with a Link AN10000 attachment for energy dispersive, x-ray analysis, in order to characterise the morphology of the samples and obtain compositional information. Stubs with sample mounts were coated with carbon and gold, the latter providing better definition for photographic reproduction.

The results of these analyses are discussed below according to sampling location.

The Green Acid Plant. Sample HB/03/001 (Figure 3 (a)) was taken from the opposite end of the pipe to sample HB/03/002, and both scales ranged between 10-15 mm in thickness. The samples are light green in colour, however, HB/03/002 had a botryoidal surface expression (Figure 4 (a)), therefore, was divided laterally into upper and lower parts, in order to examine any differences in mineralogy, and labelled HB/03/002^a and HB/03/002^b respectively.

The pipe-work at the top of the green acid plant was subject to fluorine-rich effluent, which appears in the vapours exhausted from the evaporators when the acid is concentrated. Fluorine is initially liberated as hydrogen fluoride, but in the presence of silica this readily reacts to form fluosilicic acid (H_2SiF_6), and, in the presence of other components, forms pachnolite ($NaCaAlF_6H_2O$) [15], and precipitates known in the phosphate industry as “alkali fluorosilicates” [16]. This latter material was found to be in all three samples in the form of an alkali silica hexafluoride, malladrite (Na_2SiF_6). In addition, the samples contain sodium magnesium aluminium fluoride ($NaMgAlF_6$), ralstonite ($NaMgAlF_6 \cdot H_2O$), a sublimate mineral, and iron oxide fluoride (FeOF).

Under the SEM, sample HB/03/001 appears as an aggregate composed of small spherical particles (Figure 3 (b)). Of note, is the size of these smaller particles, which are within the respirable range, *i.e.* < 10 μm, in diameter and therefore, a potential health hazard if inhaled. Sample HB/03/002^b has a more open structure compared to HB/03/001, and is also composed of particles < 10 μm in diameter, together with angular crystals growing on their surfaces (Figure 4(b)). An additional image taken of HB/03/002^b (Figure 4 (c)) shows rhombohedral crystals, > 30 μm in diameter, indicating the sample to be heterogeneous. The chemistry obtained by point analysis would suggest these crystals to be malladrite.

The Green Acid Storage Tanks. Scale sample HB/03/003 was taken from an agitator that had originally been installed in one of the storage tanks (Figure 5 (a)). This sample was hard, and displayed well defined layering of grey and black minerals; therefore, the sample was split laterally, in order to separate these two minerals for analysis, and labelled HB/03/003[a] and HB/03/003[b] respectively. Both samples were found to be predominantly gypsum ($CaSO_4 \cdot 2H_2O$). Sample HB/03/003[b] also contains small quantities of anhydrite ($CaSO_4$) and bassanite ($CaSO_4 \cdot \frac{1}{2}H_2O$), the latter known as hemihydrate in the phosphate industry.

Under the SEM, an un-separated sample of HB/03/003 shows ‘flattened’ calcium sulphate crystals, > 20 µm in diameter (Figure 5 (b)). However, it can also be seen that these crystals have, in places, become fragmented into respirable-sized particles > 10 µm.

As part of the demolition programme, the storage tanks had been cut open and the scaling scraped out and deposited around the tanks (Figure 6 (a)). This scale, HB/03/004, was extensive, and of thicknesses > 10 cm. The material is light grey in colour, and appears porous and inhomogeneous. XRD analysis found the sample to be composed of gypsum, calcium magnesium aluminium fluoride silicate ($CaMg_6Al_2Si_6O_{20}F_4$) sodium magnesium aluminium silicate fluoride ($NaMg_3AlSiO_4F_6$), sodium aluminium silicate ($NaAlSiO_4$), magnesium chloride ($MgCl_2$), and ammonium magnesium aluminium fluoride ($(NH_4)MgAlF_6$).

SEM analysis of HB/03/004 shows a mix of large, > 30 µm, gypsum crystals, and small, < 3 µm, granular particles, which, from point analysis, were determined to be calcium magnesium aluminium fluoride silicate (Figure 6 (b)).

The Purified White Acid (PWA) Plant. Sample HB/03/005 was taken from the base of the right-hand extraction column as shown in Figure 2. This soft material was found encrusted around pipe-work, and is light green in colour. From XRD analysis it was found that the material is composed of a variety of phosphate and iron compounds. These compounds are calcium phosphate ($Ca(PO_3)_2$), iron hydrogen phosphate ($FeH_2P_3O_{10}$), iron fluoride (FeF_3), collinsite ($Ca_2(MgFe)(PO_4)_2{\cdot}H_2O$), wagnerite $(Mg,Ca,Fe)_2(PO_4)F$, iron fluoride (FeF_2), iron fluoride hydrate ($FeF_2{\cdot}4H_2O$), iron phosphate ($FePO_4$) and magnesium phosphate hydrate ($Mg_3(PO_4)_2{\cdot}5H_2O$).

Sample HB/03/006^a was taken from inside the extraction column, adjacent to the solvent outflow pipe, and sample HB/03/006^b from the access door. Both samples are hard and undulate in appearance, and are approximately 2-3 mm in thickness. HB/03/006^a is cream coloured, whereas HB/03/006^b is green.

HB/03/006^a was found to be composed of all three previously encountered hydration states of calcium sulphate, *i.e.* gypsum, bassanite and anhydrite. Additional compounds that were identified are iron phosphate ($FePO_4$), aluminium hydrogen phosphate hydrate ($AlH_3(PO_4)_2{\cdot}H_2O$), aluminium chloride hydroxide hydrate ($AlCl(OH)_2{\cdot}2H_2O$) and sodium magnesium aluminium fluoride ($NaMgAlF_6$).

Sample HB/03/006^b has the same assemblage of compounds as HB/03/005 and HB/03/010; the exception being that HB/03/006^b lacks magnesium phosphate hydrate and iron phosphate ($Fe\ PO_4$). This corresponding chemical composition may be attributed to the fact that all three samples were taken from outside of the reaction vessel and at a similar level in the purifying tower (Figure 2). Sample HB/03/010 has the same appearance as HB/03/005 and was found encrusted round a stop tap.

HB/03/007 was taken from inside of the second reaction vessel (Figure 2), where it was found coating pipe work, as a hard, undulate, cream coloured deposit, approximately 4 mm in thickness. XRD analysis shows that this material is comprised of sodium magnesium aluminium fluoride ($NaMgAlF_6$) and ralstonite.

HB/03/008 is an inhomogeneous, grey/black scale, ranging between 5 mm to 10 mm in thickness, and deposited on the inside rim of the access hatch. The XRD trace obtained has a high background level suggesting the presence of an x-ray amorphous phase, which would mask this mineral identification. However, other minerals that were identified are bassanite, anhydrite and ammonium magnesium aluminium fluoride.

Sample HB/03/009 was taken from the inside of the reaction vessel, as indicated in Figure 2. Only a small (>1 g) quantity of HB/03/009 was available for sampling, as just a ‘dusting’ of vivid green crystals were found at this point. Due to the lack of material, XRD analysis was obtained by smearing the ground sample, mixed with isopropanol, onto a silicon slide. Compounds were found of ammonium iron phosphate hydrate ($(NH_4)Fe_3P_6O_{20}\cdot 10H_2O$), sodium magnesium phosphate ($Na_2Mg(PO_3)_4$) and iron fluoride hydrate ($Fe_2F_5\cdot 7H_2O$).

5. RADIOACTIVITY

Radioactivity was determined using gamma spectrometry, which utilizes a large (3800 mm^2 active area) Harwell Instruments, Broad Energy Germanium Detector with a computer equipped with software for quantitative analysis, controls data acquisition and spectral analysis. The detector was calibrated against a mixed radionuclide standard covering an energy range of approximately 50-2000 keV.

In this characterisation study, radionuclides ^{238}U ($t_{1/2}$ 4.468 x 10^9 years) and its daughters, ^{234}Pa ($t_{1/2}$ 1.18 minutes), ^{226}Ra ($t_{1/2}$ 1600 years) and ^{210}Pb ($t_{1/2}$ 22 years) were analysed, and from the ^{232}Th series, isotopes ^{228}Ra ($t_{1/2}$ 5.75 years), ^{212}Pb ($t_{1/2}$ 10.64 hours) and ^{208}Tl (3.1 minutes). Samples were prepared in the same manner as for x-ray analysis (see Section 4), and then sealed in plastic containers. Results for members of the ^{238}U decay chain are given in Table 4. The majority of the detected radioactivity is essentially from the ^{238}U decay series. None of the samples contain significant activities of the radioactive daughters of ^{232}Th due to the feedstock phosphate ore having low ^{232}Th activity (<0.01 Bq/g) [6].

As discussed in earlier, scale from the pipe sampled in the Green Acid Plant was subject to fluorine-rich effluent, and consequently the scaling was found to be comprised of fluoride-rich compounds. Uranium is readily complexed by both PO_4^{3-} and F^- ions [16], which is borne out by the ^{238}U activity found in sample HB/03/001 (8.62 Bq/g). At this location, ^{238}U has been concentrated to levels above 1.49 Bq/g encountered in the feedstock ore [6]. As expected, due to its short half-life, ^{234}Pa was found to be in equilibrium (taking into account the statistical uncertainty) with its parent ^{238}U. ^{226}Ra was also found to be enhanced in the materials from this location and in particular in samples HB/03/001 and HB/03/002^b, 0.37 Bq/g and 0.38 Bq/g respectively. ^{210}Pb is depleted relative to ^{226}Ra and, with a half-life of ~ 22 years will take approximately 100 years to reach secular equilibrium; as it takes approximately five half-lives of the daughter isotope to attain secular equilibrium with its parent.

Samples taken from the 'green acid' storage tanks are predominantly comprised of calcium sulphate. Consequently, due to the similar chemistry of radium and calcium, these materials are enriched in ^{226}Ra. In sample HB/03/003^b, ^{226}Ra and ^{210}Pb are approximately in equilibrium, as these isotopes have not been fractionated from one another during storage of the acid. Therefore, it may be concluded that both isotopes were co-precipitated with calcium sulphate, which, in this material, is present in its three hydration states. In both samples HB/03/003[a] and HB/03/004, however, ^{226}Ra has been fractionated, as it is found in excess of its daughter ^{210}Pb (Figure 7), which may be attributed to their slight differences in mineralogy, compared to HB/03/003[b] (Table 3). In addition to the enhanced ^{226}Ra level, sample HB/03/004 is a fragmentary material (Figure 6 (a)), which had been removed from the tanks and deposited over a large area around the storage facility.

Various phosphate and fluoride compounds, which have complexed 238U, dominate the deposits collected throughout the PWA plant; this is particularly apparent in samples HB/03/005 and HB/03/010, which both have the same chemical composition (Table 3). It was noted earlier that HB/03/006[b] also shares a similar composition to the aforementioned materials, however, as seen from the profiles of all three samples in Figure 7, HB/03/006[b] has a much lower ^{238}U content. This distinction is likely to be associated with its lack of iron phosphate and magnesium phosphate hydrate, which are present in both HB/03/005 and HB/03/010. Also, of particular interest is that these three samples, together with sample HB/03/006[a], have an excess of ^{210}Pb relative to its parent ^{226}Ra (Figure 7). ^{210}Pb/^{226}Ra activity levels for samples HB/03/005, HB/03/006[a], HB/03/006[b] and HB/03010 are 6.33, 1.27, 4.09 and 13 respectively. This ^{210}Pb excess must be due to direct precipitation related to the chemical reactions occurring at the corresponding stage of the purification process.

6. CONCLUSIONS

Scale samples from the Green Acid Plant, the storage tanks and the PWA plant have been characterised mineralogically and radioactively. The materials are predominantly comprised of fluorides, calcium sulphate, and an assemblage of fluorides and phosphates respectively, which can be related to the process occurring at each of these locations.

The radioactive inventory is primarily all from ^{238}U and its decay chain products. ^{238}U, and its daughter ^{234}Pa, were found to be retained in installations where the process stream was rich in fluorides and phosphates; namely the Green Acid Plant and the PWA plant. High levels of ^{226}Ra were found in association with precipitates of calcium sulphate in the storage tanks, and to a lesser extent in scales from the PWA plant. However, it was noted that many of materials from the PWA plant had ^{210}Pb activity levels in excess of its parent ^{226}Ra (Figure 7), which may be attributed to the purification process occurring in this installation.

Total inventories for radioactive elements range from 0.08 – 17.24 ± 0.07, 0.11 – 11.12 ± 0.02, 0.13 – 22.70 ± 0.08 Bq/g for U, Ra and Pb respectively (assuming short-lived (< 2 years) equilibrium between some daughter isotopes). This variation is a result of fractionation within the manufacturing process and represents differences of between 0.04 – 6.70 over the original starting materials.

These data show the detailed nature of the mineralogical and radioelement associations and are vital prerequisites for understanding the potential solubility and hence, future mobility of the elements associated with them.

REFERENCES

1. Hutchinson, D. E. & Toussaint, L. F. (1998) Near-surface Disposal of Concentrated NORM Wastes, *Applied Radiation and Isotopes. 49*, 265-271.
2. Heaton, B. & Lambley, J. (1995) TENORM, *Applied Radiation and Isotopes. 46*, 577-581.

3. Kathren, R. L. (1998) NORM Sources and Their Origins, *Applied Radiation and Isotopes. 49*, 149-168.

4. Roberts, C. J. (1998) Management and disposal of waste from sites contaminated by raioactivity, *Radiation Physics and Chemistry. 51*, 579-587.

5. Paschoa, A. S. (1998) Potential Environmental and Regulatory Implications of Naturally Occurring Radioactive Materials (NORM), *Applied Radiation and Isotopes. 49*, 189-196.

6. Poole, A. J., Allington, D. J., Baxter, A. J. & Young, A. K. (1995) The natural radioactivity of phosphate ore and associated waste products discharged into the eastern Irish Sea from a phosphoric acid production plant, *The Science of the Total Environment. 173/174*, 137-149.

7. Keating, G. E., McCartney, M. & Davidson, C. M. (1996) Investigation of the Technological Enhancement of Natural Decay Series Radionuclides by the Manufacture of Phosphates on the Cumbrian Coast, *Journal of Environmental Radioactivity. 32*, 53-66.

8. McCartney, M., Davidson, C. M., Howe, S. E. & Keating, G. E. (2000) Temporal changes in the distribution of natural radionuclides along the Cumbrian coast following the reduction of discharges from a phosphoric acid production plant, *Journal of Environmental Radioactivity. 49*, 279-291.

9. FSA/SEPA. (2001) Radioactivity in Food and the Environment in pp. 45-101, Food Standards Agency/Scottish Environmental Protection Agency,

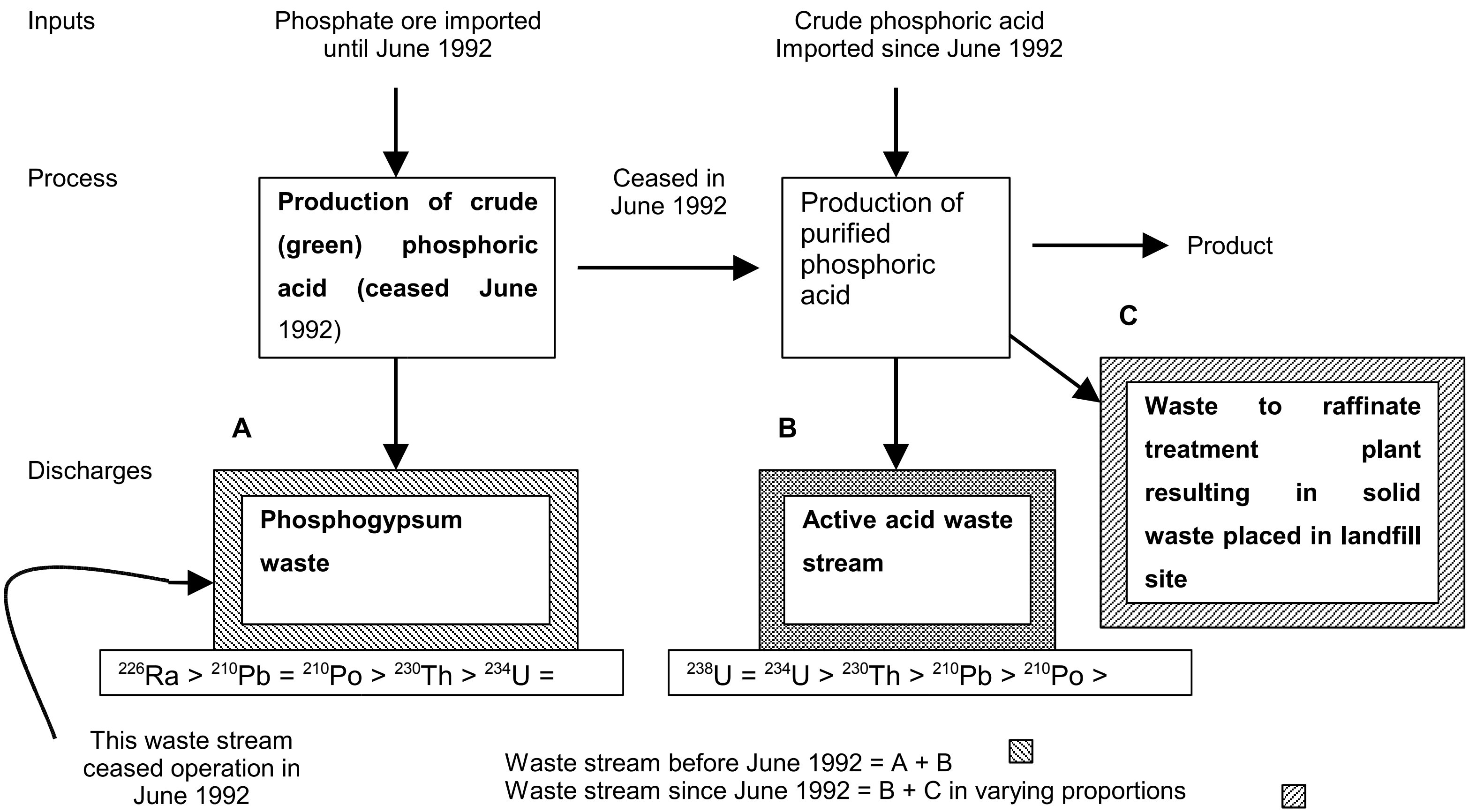
10. Rutherford, P., Dudas, M. & Arocena, J. (1996) Heterogeneous distribution of radionuclides, barium and strontium in phosphogypsum by-products, *The Science of the Total Environment. 180*, 201-209.

11. EC. (2003) Draft Reference Document on Best Available Techniques in the Large Volume Inorganic Chemicals, Ammonia, Acids and Fertilisers Industries in pp. 98-102, European Commission,

12. EFMA. (2000) Production of Phosphoric Acid: Best Available Techniques for Pollution Prevention and Control in the European Fertiliser Industry in, European Fertiliser Manufacturers' Association.

13. Tucker, M. E. (1995) *Sedimentary Petrology*, Blackwell Science.
14. Schrodter, K. (1998) *Industrial Inorganic Chemicals and Products*, Wiley-VCH.
15. Upchurch, S. B., Rea, R. A. & Stevenson, R. G. (1982) Sedimentary pachnolite and fluorite from Tampa Bay, Florida, *American Mineralogist. 67*, 1258-1264.
16. Burnett, W. C. & Elzerman, A. W. (2001) Nuclide migration and the environmental radiochemistry of Florida phosphogypsum, *Journal of Environmental Radioactivity. 54*, 27-51.

TABLE OF FIGURES



Inputs

Phosphate ore imported until June 1992

Crude phosphoric acid Imported since June 1992

Process

Production of crude (green) phosphoric acid (ceased June 1992)

Ceased in June 1992

Production of purified phosphoric acid

Product

C

Waste to raffinate treatment plant resulting in solid waste placed in landfill site

A

B

Discharges

Phosphogypsum waste

Active acid waste stream

$^{226}\mathrm{Ra} > {}^{210}\mathrm{Pb} = {}^{210}\mathrm{Po} > {}^{230}\mathrm{Th} > {}^{234}\mathrm{U} =$

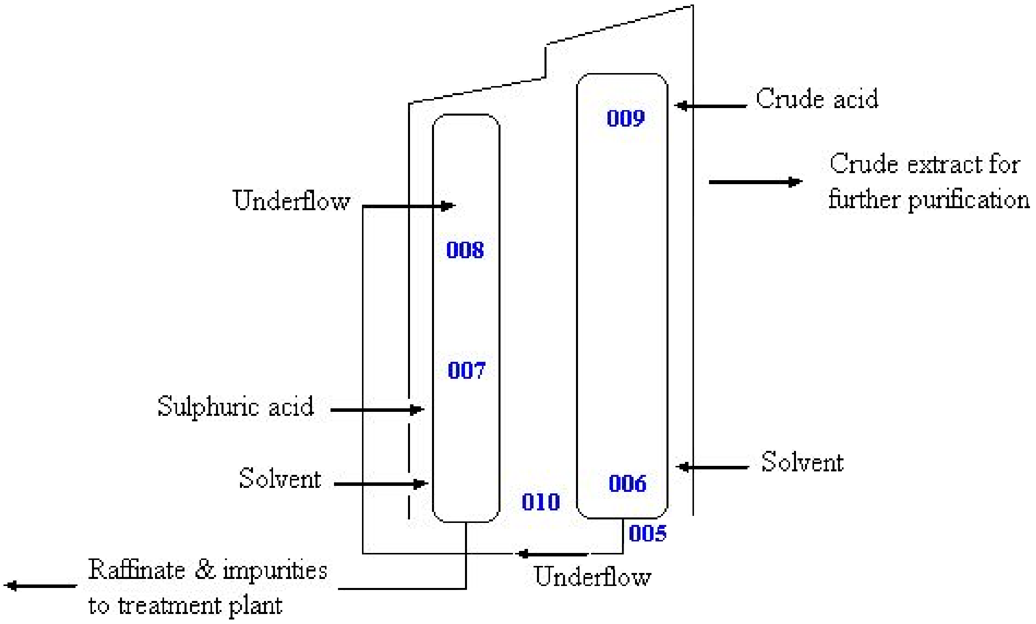
$^{238}\mathrm{U} = {}^{234}\mathrm{U} > {}^{230}\mathrm{Th} > {}^{210}\mathrm{Pb} > {}^{210}\mathrm{Po} >$

This waste stream ceased operation in June 1992

Waste stream before June 1992 = A + B ▧
Waste stream since June 1992 = B + C in varying proportions ▨

Figure 1

Figure 2


Crude acid
009
Crude extract for further purification
Underflow
008
007
Sulphuric acid
Solvent
010
006
Solvent
005
Raffinate & impurities to treatment plant
Underflow

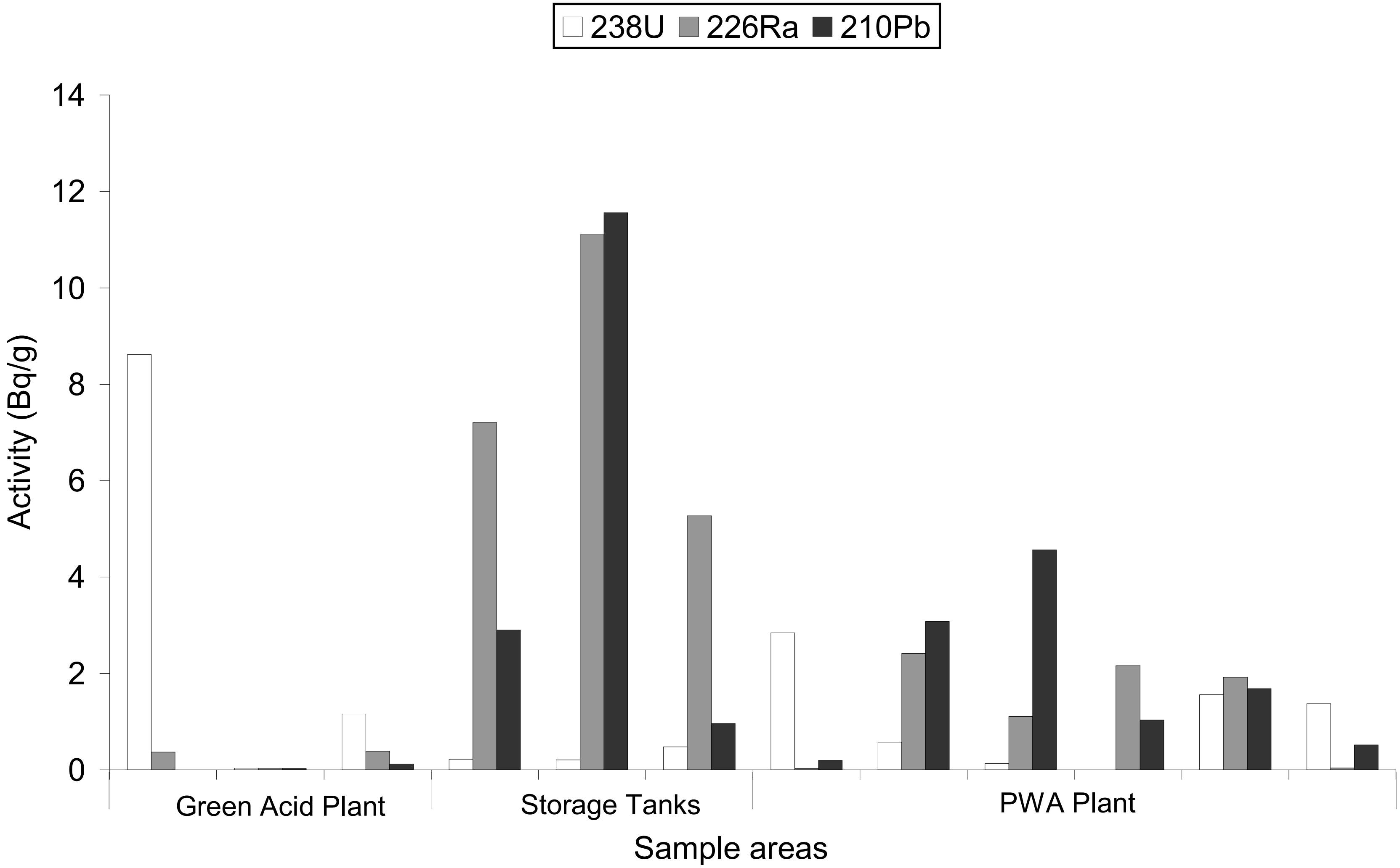

☐ 238U
▨ 226Ra
■ 210Pb
14
12
10
8
6
4
2
0
Activity (Bq/g)
Green Acid Plant
Storage Tanks
PWA Plant
Sample areas

TABLE OF TABLES

Industry	**Location**	**Contamination**	**Aerial Extent**	**Institutional Control**	**Nature of the Hazard**
Coal Fired Power Station.	Drax & Eggborough, Leeds.	^{238}U, ^{232}Th & decay chain products. ^{210}Pb & ^{210}Po follow airborne pathways.	Not known.	Emissions to air considered below the UK regulations, however, future restrictions may be put on the uses of coal ash.	Contaminates are concentrated in the furnace flue and coal ash consisting of fly ash, bottom ash & boiler slag.
Mineral Processing	Cornwall & Devon	^{226}Ra & ^{228}Ra	Various process plant	Managed site	Insoluble Ra-substituted barite plated out on process installations.
MoD.	Fife.	^{226}Ra.	Beach and foreshore.	Managed site.	Incinerated radium luminised dials.
Oil & Gas.	Aberdeen.	^{226}Ra, ^{228}Ra, ^{210}Pb & ^{210}Po.	Not known.	Managed site.	Macerated solid material discharged to sea.
Paint Manufacturer	Gowkthrapple Wishaw, Scotland	^{226}Ra	Areas within 6 hectares	Managed site	Buried radium paints
Phosphoric Acid.	North of England	^{238}U, ^{232}Th & decay chain products.	Not known.	Managed site.	Liquid slurry discharged to sea. Ufex and radioactive plant landfilled on site.
Radium Extraction	Loch Lomond.	^{226}Ra	'Hot spots' within a 30 x 50 m area	Managed site	Radium extraction company.
Refractory Metals.	Brighton.	^{238}U & ^{232}Th	Not known.	Not known.	Particles of rare earth oxides produced during grinding of electrodes.
Special Precautions Burial.	Whittle Hill quarry, Preston.	^{238}U	Not known.	Not known.	Solid waste e.g. drums used for transporting uranium ore, contaminated brickwork, laboratory ware etc.

TABLE 1

	CEI Russia*	S. AFRICA Palabora*	MOROCCO Khouribga	USA Florida	SENEGAL	Certified Standard[1]
Composition (wt %)						
P_2O_5	38.9	36.8	33.4	34.3	36.7	36.04
CaO	50.5	52.1	50.6	49.8	50	55.74
Na_2O	0.4	0.1	0.7	0.5	0.3	0.1
MgO	0.1	1.1	0.3	0.3	0.1	0.83
Al_2O_3	0.4	0.2	0.4	1.1	1.1	<LLD
SiO_2	1.1	2.6	1.9	3.7	5.0	0.37
K_2O	0.5	0.1	0.1	0.1	0.1	<LLD
Fe_2O_3	0.3	0.3	0.2	1.1	0.9	<LLD
CO_2	0.2	3.5	4.5	3.1	1.8	NR
SO_3	0.1	0.2	1.6	0.1	NR	NR
F^-	3.3	2.2	4.0	3.9	3.7	NR
Cl^-	NR	NR	0.1	NR	NR	NR
Organics	NR	0.1	0.3	0.5	NR	NR
Organ. C	0.1	NR	NR	0.2	0.4	NR
Trace elements (ppm)						
Rare earth elements	6200	4800	900	600	NR	5745
As	10	13	13	11	18	24
Cd	1.2	1.3	15	9	53	<LLD
Cr	19	1	200	60	6	<LLD
Cu	37	102	40	13	NR	76
Hg	33	0.1	0.1	0.02	0.2	NR
Ni	2	2	35	28	NR	15
Pb	NR	11	10	17	5	20
Sr	29000	3000	1000	NR	NR	4000
U	11	134	185	101	124	189
Zn	20	6	200-400	70	NR	<LLD

TABLE 2

*Igneous

[1] Phosphate rock standard from Palabora, S. Africa, analysed at Reading University

<LLD Less than the lowest limit of detection

NR = Not reported

Location	Green Acid Plant			Storage Tanks			PWA Plant						
HB/03/-	001	002[a]	002[b]	003[a]	003[b]	004	005	006[a]	006[b]	007	008	009	010
Sodium Magnesium Aluminium Fluoride	•	•	•					•		•			
Ralstonite ($NaMgAlF_6 \cdot H_2O$)	•	•	•							•			
Malladrite (Na_2SiF_6)	•	•	•										
Iron Oxide Fluoride	•	•	•										
Gypsum ($CaSO_4 \cdot 2H_20$)				•	•	•							
Bassanite ($CaSO_4 \cdot 0.5H_20$)					•			•			•		
Anhydrite ($CaSO_4$)					•			•			•		
Calcium Magnesium Aluminium Fluoride Silicate						•		•					
Sodium Magnesium Aluminium Silicate Fluoride						•							
Sodium Aluminium Silicate						•							
Magnesium Chloride						•							
Ammonium Magnesium Aluminium Fluoride						•					•		
Calcium Phosphate							•		•				•
Iron Hydrogen Phosphate							•		•				•
Iron (III) Fluoride							•		•				•
Collinsite ($Ca_2(Mg,Fe)(PO_4)_2 \cdot 2H_2O$)							•		•				•
Wagnerite ($(Mg,Ca,Fe)_2(PO_4)F$)							•		•				•
Iron (II) Fluoride							•		•				•
Iron Fluoride Hydrate							•		•				•
Iron Phosphate							•	•					•
Magnesium Phosphate Hydrate							•						•
Aluminium Chloride Hydroxide Hydrate								•					
Aluminium Hydrogen Phosphate Hydrate								•					
Ammonium Iron Phosphate Hydrate												•	
Sodium Magnesium Phosphate												•	
Iron Fluoride Hydrate												•	

TABLE 3

Location	Sample	^{238}U (± %)	^{234}Pa (± %)	^{226}Ra (± %)	^{210}Pb (± %)
		Bq/g			
Green Acid Plant	HB/03/001	8.62 (0.79)	9.35 (3.10)	0.37 (1.31)	< LLD
	HB/03/002^{a}	0.04 (2.66)	< LLD	0.03 (0.92)	0.03 (2.00)
	HB/03/002^{b}	1.16 (1.22)	1.44 (8.38)	0.38 (1.00)	0.12 (4.22)
Storage Tanks	HB/03/003^{a}	0.22 (8.35)	< LLD	7.21 (0.23)	2.90 (0.62)
	HB/03/003^{b}	0.21 (15.75)	< LLD	11.11 (0.37)	11.55 (0.98)
	HB/03/004	0.48 (10.89)	< LLD	5.27 (0.34)	0.96 (7.57)
PWA Plant	HB/03/005	2.84 (0.94)	4.69 (7.36)	0.03 (6.25)	0.19 (8.37)
	HB/03/006^{a}	0.58 (9.38)	< LLD	2.42 (0.60)	3.08 (3.00)
	HB/03/006^{b}	0.14 (12.76)	< LLD	1.11 (1.21)	4.55 (1.47)
	HB/03/007	< LLD	< LLD	2.16 (0.57)	1.04 (6.37)
	HB/03/008	1.56 (3.14)	1.98 (12.89)	1.93 (0.60)	1.68 (3.81)
	HB/03/010	1.37 (1.33)	2.17 (11.81)	0.04 (5.56)	0.52 (3.59)
	Standard[1]	0.10 (2.59)	< LLD	0.12 (0.66)	0.05 (2.44)

TABLE 4

[1] Phosphate rock standard, of igneous origin, from Palabora, South Africa.
< LLD Less than the lowest limit of detection

IN SITU GAMMA-RAY SPECTROMETRY IN COMMON ROCK RAW MATERIALS MINED IN KRAKOW VICINITY, POLAND

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Abstract

The natural radioactivity of ^{40}K, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{228}Ac and the fallout of ^{137}Cs in common rock raw materials mined in Krakow vicinity were measured *in situ* using a portable gamma-ray spectrometry workstation. The measurement points were chosen for different regional rocks in: Devonian and Jurassic limestones, dolomite, trachyandesite, porphyry, porphyry tuff, diabase and melaphyre. ^{40}K activity varied in the range from about 82 Bqkg^{-1} (Jurassic limestone) to 3150 Bqkg^{-1} (porphyry tuff). The activity concentrations associated with ^{228}Ac (^{232}Th series) varied in the range from 9 Bqkg^{-1} (Jurassic limestone) to 56 Bqkg^{-1} (porphyry tuff), whereas activity of ^{226}Ra (^{238}U series) ranged from about 13 Bqkg^{-1} (Jurassic limestone) to 43 Bqkg^{-1} (Devonian limestone). The highest deposition of ^{137}Cs (20 kBqm^{-2}) was recorded in Devonian limestone.

Keywords

Tuff, limestone, dolomite, diabase, melaphyre, trachyandesite, porphyry, rock raw materials Krakow, in situ gamma-ray spectrometry, natural radioactivity

Introduction

Krakow surroundings are one of the places where human settlement started in central part of Europe. This region has been numbered among the densest populated areas in Poland for centuries. Favorable geological features have enabled local communities to mine rocks in great variety and use them as raw materials for building purposes since the early Middle Ages. Presently, some of the local rocks are exploited on a commercial scale and the output supplies home industry serving as mineral raw materials for many fields of production. In the current study the natural radioactivity of ^{40}K, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{228}Ac and the fallout of ^{137}Cs were measured *in situ* in common rock raw materials mined in Krakow vicinity, using a portable gamma-ray spectrometry workstation.

Geological setting and measurement locations

Study area occupies the south-east edge of regional geological unit called silesian-krakowian monocline (SKM). The SKM forms a layered plate whose upper complex consists of Permian-to-Cretaceous rocks inclined towards the north-east. Aside from the regional direction of dip, the southern part of the monocline subsides in steplike manner, being partially overthrusted by the Carpathians, which emerged in the south, and partially included in vast tectonic depression of the Carpathian Foredeep (Fig. 1). The older formation, which underlies Mesozoic complex of the SKM, was folded and faulted during Carboniferous-to-Permian tectonic episode. Elevations of that time were flattened out subsequently and the plain was covered consecutively by Permian, Triassic, Jurassic and Cretaceous deposits. Monoclinal features of the rockmass originated at the end of the Cretaceous period when both lower and upper complexes were tilted to the north-east direction. In the Palaeogene when the SKM area remained a land, its southern part, as the most uplifted, was subjected to extensive denudation. Long-lasting erosion resulted in removal of thick series of rock cover and made exposed older formations in Krakow neighborhood (see Fig. 1). Tectonic activity in the Neogene expressed as folding within collisional orogeny of the Carpathians south of Krakow area. Large scale northwards overthrusts of orogenic units resulted in concurrent faulting of the overloaded foreland where number of horst and grabens formed. The marine transgression onto newborn tectonic depressions in front of the Carpathian belt took place in the Miocene. One of such down-dropped blocks crosses outskirts of Krakow town. This narrow west-east elongated depression called the Krzeszowice graben (Fig. 1) is limited by roughly parallel normal faults. Footwalls of the faults are typical places where the formations belonging to both lower and upper complexes of the SKM crop out. Most exposed rocks are considered as highly valued raw materials. Their outcrops were selected as sites for conducting the field measurement of radioactivity levels in rocks with gamma-ray spectroscopy. The sites are described below in stratigraphical order starting from the oldest rocks.

Point 1 (see Fig. 1) was established in the Dubie quarry. Dolomites, which are mined there, resulted from Variscan dolomitisation of coral and stromatoporoid limestones deposited during the Lower Givetian period. They make up the oldest formation that surfaces in the SKM. Building aggregates produced by the Dubie quarry are mainly used as crushed stones for road pavements. Measurement in the Debnik quarry (see Fig. 1, point 2) was done for bituminous limestone of Upper Givetian age. This site is the only black limestone occurrence in Poland, which has been exploited since 1415. Rawblocks of this attractive high-quality “marble” are in great demand at domestic market.

Felsic subvolcanic rocks here and there intrude Devonian carbonates (points 1 and 2) during the Upper Carboniferous and Lower Permian periods. Site 3 (see Fig. 1) was located on trachyandesite dyke, which cut vertically dolomite complex in the Dubie quarry. This rock, according to its chemical properties, was used as a ceramic material. Where the volcanites approached ground surface, felsic lava flows of Variscan age formed. Now they are exposed in both southern and northern edges of the Krzeszowice graben. One of those outcrops is the Miekinia quarry where porphyry mined since 1852 (see Fig. 1, point 4) lies on Lower Permian continental deposits. The main Miekinia products were building and paving stones as well as porphyry elements of small architecture. Porphyry tuff, which is common loose material coming from felsic volcanic eruptions, occurs near Filipowice. This tuff has for ages served as an important local building stone. The Kowalska Gora closed quarry of the Filipowice tuff was another place chosen for present measurement (see Fig. 1, site 5).

Apart from the felsic one there is also mafic igneous formation originated during Variscan folding of the SKM lower complex. Point 6 (see Fig. 1) was established where diabase crops out near the Niedzwiedzia Gora quarry. A syntectonic sill of hypersthene-quartz diabase intruded there the Upper Carboniferous clastic sediments. The diabase, got since 1910, is regarded as very good raw material for aggregates used in road construction industry. A volume of mafic lava-flows remained from the same episode of magma genesis. From among them an outcrop of Lower Permian melaphyre at the Regulice closed road-stone quarry (see Fig. 1, site 7) was selected to perform present measurement. Point 8 (see Fig. 1) was localized in the Nielepice quarry, which mines the most common raw material belonging to the upper complex of the SKM. This is Upper Jurassic platy limestone; formerly traditional building stone used to construct most of medieval monuments in southern Poland, currently used mainly for cement and lime production.

For more detailed information on geology and rock raw materials of Krakow area paper of Kozlowski (1990) as well as Geology of Poland (1970, 1976 and 1977) can be recommended.

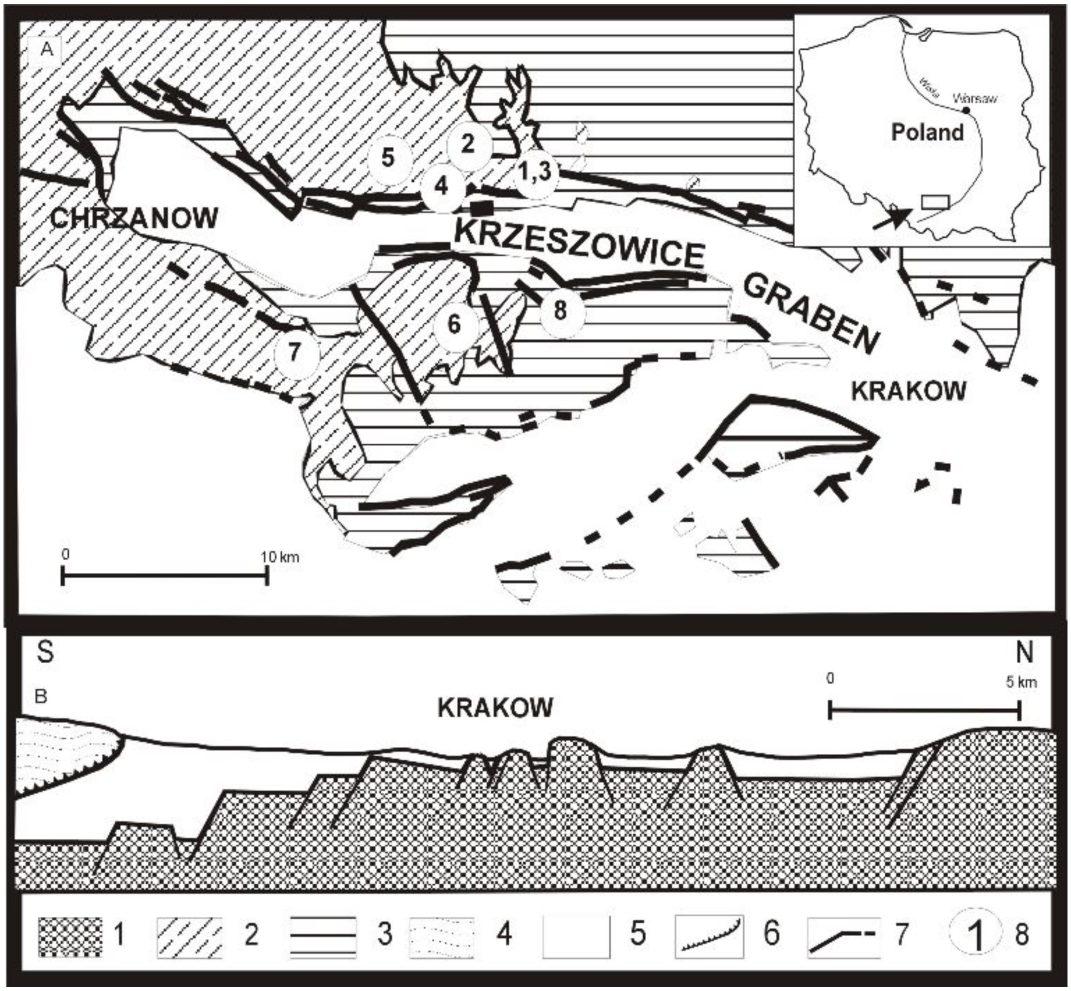

Fig. 1. General outline of the study area (after Gradzinski, 1972) showing measurement locations. A. geological map, B. synthetic cross-section.

1 - Palaeozoic and Mesozoic formations (not distinguished), 2 - Palaeozoic rocks, 3 - Mesozoic complex, 4 - the Carpathian folded units, 5 - Miocene marine sediments of the Carpathian Foredeep, 6 - the Carpathian orogeny front, 7 - main faults, 8 - locations of field measurements

Methods

The system (EG&G ORTEC) consists of a HPGe detector (30% efficiency, crystal length: 59 mm, diameter: 58.6 mm) with cryostat PGM-5 (liquid nitrogen) mounted on a tripod, a multichannel buffer DART, and a laptop. The manufacturer’s quoted resolutions of the detector are 0.67 keV at 122 keV and 1.73 keV at 1.33 MeV.

Software used for determination of the radionuclides M-1-B32 (EG&G ORTEC) - implements the one–meter geometry, *in situ* analysis methods developed by the U.S. DOE Environmental Measurements Laboratory (Beck et al, 1972). The software is divided into two main parts: the supervisor program which uses the programs M-1 Setup and Gamma Vision-32, and the operator program M-1 for Windows. In field conditions, the detector was mounted 1 m above the rock and, in the case, detector view for gamma emitters was approximately 10 m in radius to a depth of ca 30 cm, depending on the ground and the energy source (Helfer and Miller, 1988). For the determination of the presence of discrete radionuclides and calculations of their activities the following gamma-ray transitions (in keV) were chosen: ^{7}Be (477), ^{40}K (1460.8), ^{137}Cs (661.7), ^{208}Tl (510.8, 583.1 and 860.5), ^{212}Pb (238.6 and 300.1), ^{212}Bi (727.2 and 1620.6), ^{214}Pb (241.9, 295.2 and 351.9), ^{214}Bi (609.3, 1120.3, 1238.1 and 1764.5) and ^{228}Ac (338.3, 911.1 and 968.9) (Debertin and Helmer, 1988). The energy tolerance for library file (1Meter.lib) was stated as 1.75 keV. Counting time was set for 3 h for each measured location. The energy calibration of the spectrometer was carried out using powdered mixture ^{40}K (840 Bq), ^{226}Ra (218 Bq) and ^{232}Th (127 Bq) calibration sources. The vertical distribution of particular radionuclides is described within M-1 software by parameter α/ρ, where α is the reciprocal of the relaxation length (flux reduction by factor *e*) for the gamma energy line being observed (cm^{-1}) and ρ is the soil (rock) density (gcm^{-3}) (EG&G ORTEC, 2000). Three cases represent the general source distribution: $\alpha/\rho < 0.1$, uniform source distribution (natural radionuclides), $\alpha/\rho > 0.5$, planar source distribution (fresh fallout) and $0.1 < \alpha/\rho < 0.5$, not uniform or planar. Values of α/ρ ranging from 0.1 to 0.5 have been found to describe realistic fallout distributions adequately, the more aged fallout will be represented by the smaller values. In our work we assumed $\alpha/\rho = 0$ for distributions of ^{40}K, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi and ^{228}Ac whereas for ^{137}Cs $\alpha/\rho = 0.21$ (manufacturer's recommended values), EG&G ORTEC (2000) and ORTEC (2000).

Results and Discussion

The results of *in situ* γ-ray measurements of ^{40}K, ^{137}Cs, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{228}Ac and calculated activity concentration of ^{226}Ra at all measurement locations are given in Table 1. The total uncertainty value (Tab. 1) consists of the random and systematic errors in all of the factors involved in calculating the final nuclide concentration result (ORTEC, 2000). The error can be expressed as:

$$\sigma_t = \sqrt{\sum \sigma_{ri}^2 + \frac{1}{3}\sum \sigma_{si}^2} \qquad (1)$$

where: σ_t is the total uncertainty, σ_{ri} is the individual random error and σ_{si} is the individual systematic error. The random uncertainties are counting, random summing and absorption correction, whereas the systematic uncertainties are nuclide uncertainty from library, efficiency fitting uncertainty, calibration source uncertainty and geometry correction. The random summing uncertainty is estimated to be 10% of the Eq. 1 (ORTEC, 2000).

Table 1. The results of *in situ* γ-ray measurements of ^{40}K, ^{208}Tl, ^{137}Cs, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi and ^{228}Ac at different locations in the Krakow vicinity. The uncertainty means one standard deviation (σ_t), Eq. 1.

Nuclide	Activity (Bqkg^{-1})							
	Measurement locations							
	1	2	3	4	5	6	7	8
^{137}Cs*	< 66	20165 ± 168	< 66	8830 ± 188	3499 ± 133	1037 ± 95	7878 ± 168	< 66
^{40}K	85 ± 4	473 ± 9	184 ± 3	1032 ± 6	3154 ± 15	531 ± 6	1215 ± 10	82 ± 3
^{208}Tl	2.4 ± 0.3	11.4 ± 0.9	3.3 ± 0.6	14.2 ± 0.9	17.3 ± 1.7	13.2 ± 2.1	20.6 ± 0.7	3.4 ± 0.5
^{212}Pb	< DL	30.3 ± 0.8	6.9 ± 0.4	38.8 ± 0.8	37.2 ± 1	33.4 ± 0.7	49.2 ± 1	7.8 ± 0.3
^{212}Bi	< DL	< DL	< DL	29.4 ± 3.7	< DL	41.5 ± 8.7	< DL	4.6 ± 0.7
^{228}Ac	7.2 ± 1.3	30.9 ± 5.6	9.7 ± 1.7	38.6 ± 4.4	55.9 ± 6.9	35.2 ± 5.2	55.3 ± 7.2	9.5 ± 2
^{214}Pb	20.3 ± 2.6	42.2 ± 4.8	23.6 ± 4.8	23.8 ± 2.2	34 ± 3.2	28.3 ± 3.4	30.1 ± 3.2	13.7 ± 1.8
^{214}Bi	18.1 ± 3.3	44.3 ± 6.7	20.4 ± 5.7	23.2 ± 5	31.4 ± 5.7	30.2 ± 3.9	25.8 ± 4.5	11.9 ± 2.7
^{226}Ra**	19.2 ± 3.7	43.2 ± 6.8	22 ± 6.4	23.5 ± 4.5	32.7 ± 5.5	29.2 ± 4.4	27.9 ± 5.1	12.8 ± 2.8

* Bq/m^2

** Based on ^{214}Bi and ^{214}Pb activities

DL - detection limit

^{40}K

The highest activity concentrations of ^{40}K were noted in porphyry tuff, 3154 Bq/kg (point 5), melaphyre 1215 Bqkg^{-1} (point 7) and porphyry 1032 Bqkg^{-1} (point 4). The lowest activity concentrations of ^{40}K were measured in Jurassic limestone, 82 Bqkg^{-1} (point 8), dolomite 85 Bqkg^{-1} (point 1) and trachyandesite 184 Bqkg^{-1} (point 3). Intermediate values refer to the Devonian limestone, 473 Bqkg^{-1} (point 2) and diabase, 530 Bqkg^{-1} (point 6). In Fig 3 the comparison of ^{40}K activity concentration in rocks of studied area with average concentrations in soil and continental crust is shown. As can be seen in Fig. 3, extremely high concentration of ^{40}K was measured in porphyry tuff, nearly fourth and eight times higher than average ^{40}K activity concentrations for continental crust and soil i.e., 850 Bqkg^{-1} and 400 Bqkg^{-1}

respectively (Eisenbud and Gesell, 1997). Activity concentrations of ^{40}K that are distinctly higher than crustal and soil averages are visible in melaphyre and porphyry. The concentration levels of ^{40}K clearly below the continental crust and soil averages are characteristic for Jurassic limestone, dolomite and trachyandesite (Fig. 2).

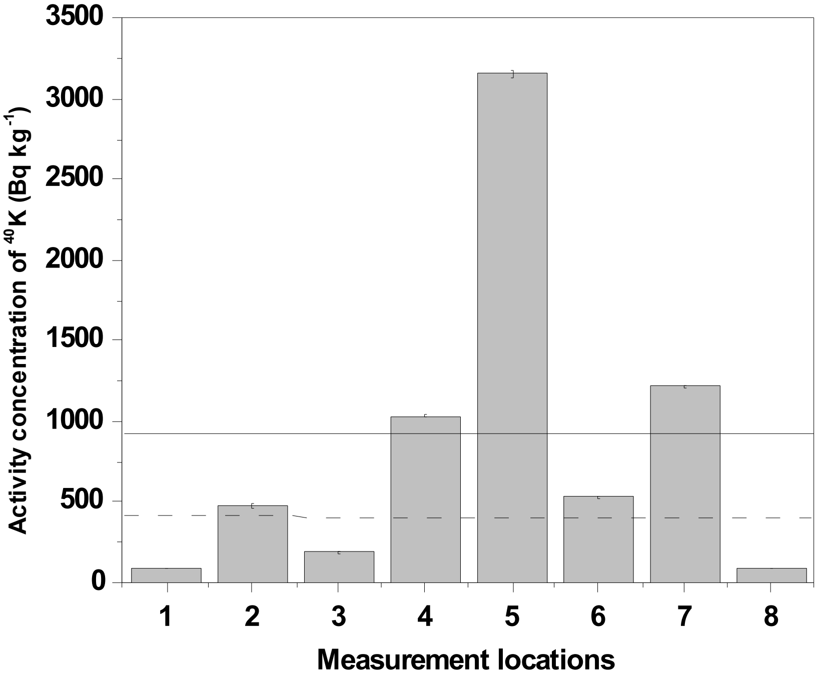

Fig. 2. Comparison of the ^{40}K activity concentrations (grey bars) with average activities reported for continental crust (solid line) and soil (dashed line) for each measurement location in the Krakow vicinity.

^{137}Cs

The measurements in the Krakow vicinity have shown diverse levels of ^{137}Cs fallout activity after Chernobyl accident and weapon tests, ranged from 20165 Bqm^{-2} in Devonian limestone (point 2) to less than 66 Bqm^{-2} in dolomite (point 1), trachyandesite (point 3) and Jurassic limestone (point 8, Fig. 3 and Tab.1). Such low depositions of ^{137}Cs in these rocks are due to the removal of superficial layer during exploitation of these quarries. As mentioned above, definitely the highest depositions of ^{137}Cs were noted at point 2 (Fig. 3) in Devonian limestone, then at points: 4 (porphyry, 8829 Bqm^{-2}), 7 (melaphyre, 7877 Bqm^{-2}), 5 (porphyry tuff, 3498 Bqm^{-2}) and 6 (diabase, 1037 Bqm^{-2}). These depositions agree well with the deposition of ^{137}Cs for this part of Poland, ranging from 3 to 20 $kBqm^{-2}$, reported by the Polish Central Laboratory for Radiological Protection (Jagielak et al, 1998).

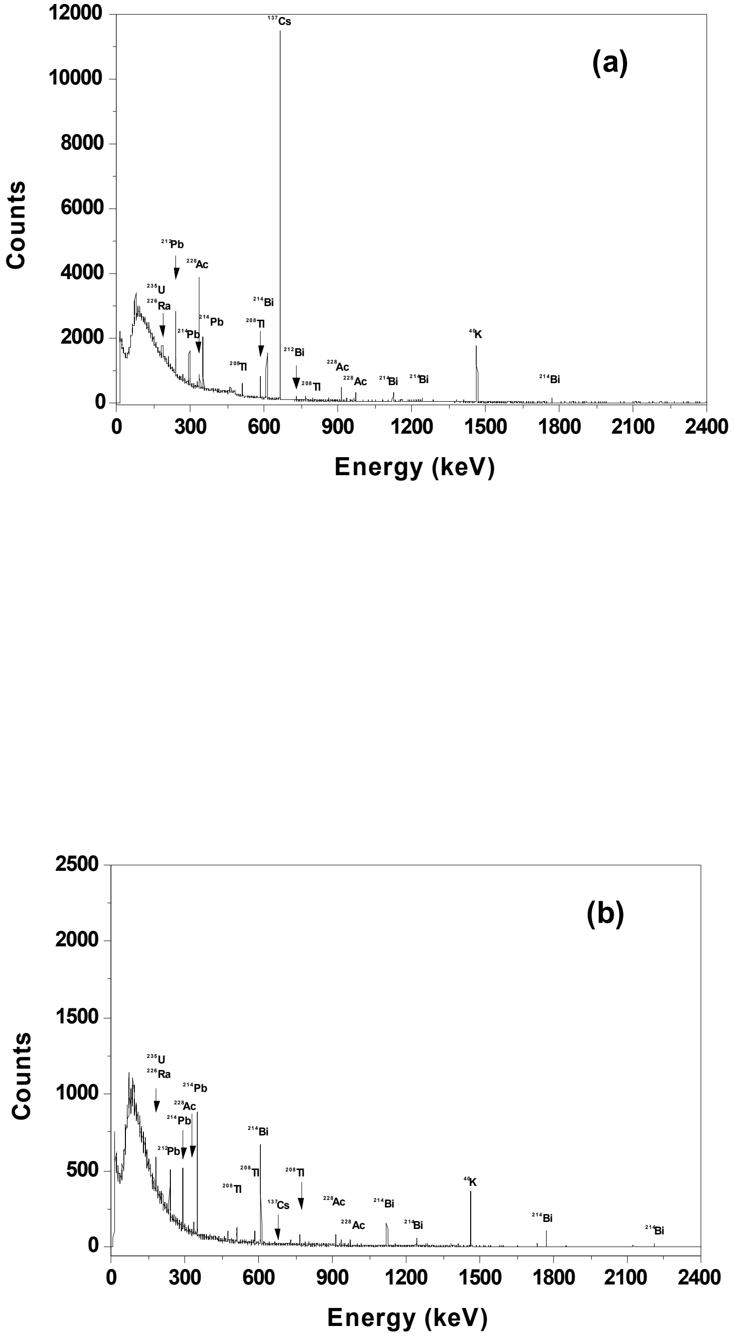

Fig. 3. *In situ* γ–ray spectra obtained with the portable gamma-ray spectrometry from: (a) Devonian limestone and (b) Jurassic limestone. The characteristic γ-ray emitters are marked above the corresponding peaks. The spectrum of Jurassic limestone does not show the characteristic 661.7 keV line from ^{137}Cs.

^{232}Th series (^{228}Ac, ^{212}Pb, ^{212}Bi and ^{208}Tl)

As is shown in Tab. 1, there is an excellent radioactive equilibrium between ^{228}Ac and ^{208}Tl in ^{232}Th series at each measurement location. The activity concentrations associated with ^{228}Ac are the highest in porphyry tuff (point 5, Tab.1) and in melaphyre (point 7). Intermediate concentrations of ^{228}Ac, 38.6 Bqkg^{-1}, 35.2 Bqkg^{-1} and 30.9 Bqkg^{-1} were noted in porphyry (point 4), diabase (point 6) and Devonian limestone (point 2) respectively. Activities of ^{228}Ac < 10 Bqkg^{-1} were recorded in dolomite (point 1), trachyandesite (point 3) and Jurassic limestone (point 8).

^{226}Ra (^{214}Pb, ^{214}Bi)

Activity concentrations of ^{226}Ra at the locations 6, 7, 4, 3 and 1 (Fig. 1, Tab. 1) vary in relatively narrow range between 29.9 Bqkg^{-1} (diabase, point 6) and 19.2 Bqkg^{-1} (dolomite, point 1). The highest concentrations of ^{226}Ra, 43.2 Bqkg^{-1} and 32.7 Bqkg^{-1} were noted in Devonian limestone (point 2) and porphyry tuff (point 5) respectively, whereas the lowest value 12.8 Bqkg^{-1} was recorded in Jurassic limestone.

Activity concentrations of ^{232}Th and ^{238}U

In this work we assumed the radioactive equilibrium in ^{232}Th → ^{228}Ac and ^{238}U →^{226}Ra →^{222}Rn → ^{214}Pb → ^{214}Bi series. In relation to ^{214}Pb and ^{214}Bi, exhalation of ^{222}Rn from the soil (rock) can produce 10-20% reduction in the gamma-emitting ^{214}Pb and ^{214}Bi on the surface. However in the field measurements the exhalation of ^{222}Rn is compensated in most part by the contribution of the flux from the same nuclides in the ambient air (Helfer and Miller, 1988). Based on these assumptions, the activity concentrations of ^{232}Th and ^{238}U in rocks of the Krakow vicinity are shown in Fig. 4. As can be seen in Fig. 4 at two points: 5 (porphyry tuff) and 7 (melaphyre), the concentrations of ^{232}Th exceed the concentration of this nuclide in continental crust, i.e., 44 Bqkg^{-1} (Van Schmus, 1995; Eisenbud and Gesell, 1997). All other locations are characterized by concentrations lower than mentioned mean for thorium. In case of ^{238}U, only Devonian limestone (point 2) clearly exceeds the average uranium concentration, 36 Bqkg^{-1}, reported for continental crust. All other measured rocks showed ^{238}U concentration below the continental crust's value (Fig. 4).

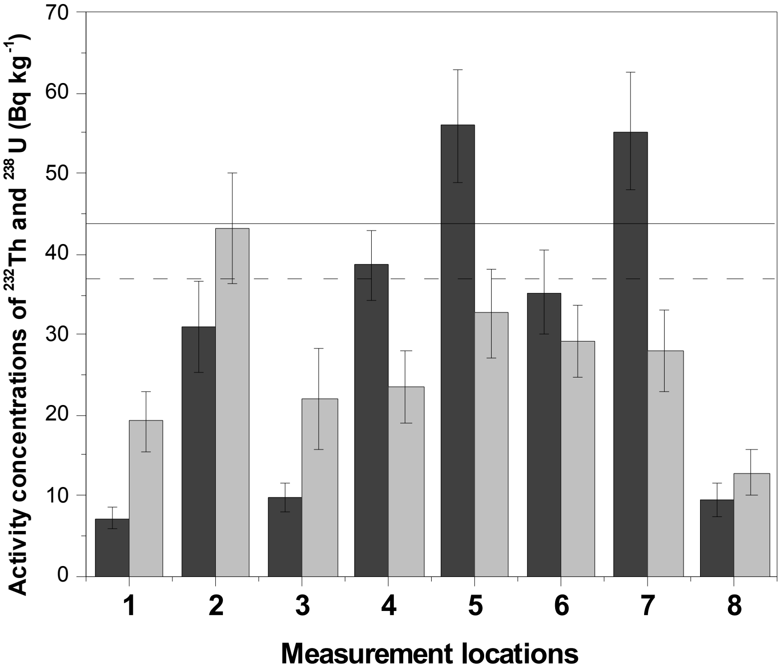

Fig. 4. Comparison of the ^{232}Th and ^{238}U activity concentrations (black and grey bars respectively) obtained *in situ* in common rock raw materials in the Krakow vicinity with average activities reported for these nuclides in continental crust. Solid line – the average crustal concentration of ^{232}Th, dashed line – the average crustal concentration of ^{238}U.

Conclusions

In situ γ-ray spectrometry appears to be a useful tool for obtaining actual concentrations of radionuclides in the environment. According to the results reported in this paper, some of the rocks from the Krakow vicinity are characterized by increased concentration of ^{40}K (porphyry tuff, melaphyre and porphyry), ^{232}Th (porphyry tuff and melaphyre) and ^{238}U (Devonian limestone) in comparison with continental crust's averages for these nuclides. The ^{137}Cs fallout measurements show deposition of this nuclide varying in wide range from 20 kBqm^{-2} (Devonian limestone) to less than 66 kBqm^{-2} (dolomite, trachyandesite and Jurassic limestone).

References

Beck, H. L., De Campo, J. & Gogolak, C. V. (1972). *In situ Ge(Li) and Na(Tl) gamma-ray spectrometry.* U.S. Department of Energy, Environmental Measurements Laboratory, HASL-258, New York.

Debertin, K. & Helmer, R. G. (1988). *Gamma- and X-ray spectrometry with semiconductor detectors.* Elsevier, Amsterdam.

EG&G ORTEC (2000). *In Situ Spectroscopy M-1-B32 M-1 Setup Supervisor Program*. Software User's Manual. EG&G ORTEC Part No. 779980, Oak Ridge.

Eisenbud, M. & Gesell, T. (1997). *Environmental radioactivity from natural, industrial, and military sources.* Academic Press, San Diego, 134 - 200.

Geology of Poland (1970). *Stratigraphy. Part 1: Pre-Cambrian and Palaeozoic.* Wyd. Geol., Warszawa.

Geology of Poland (1976). *Stratigraphy. Part 2: Mesozoic.* Wyd. Geol., Warszawa.

Geology of Poland (1977). *Tectonics.* Wyd. Geol., Warszawa.

Gradzinski, R. (1972). *Krakow vicinity, geological guidebook* (in Polish). Wyd. Geol., Warszawa.

Helfer, I. K. & Miller, K. M. (1988). Calibration factors for Ge detectors used for field spectrometry. *Health Phys.* **55**, 15-29.

Jagielak, J., Biernacka, M., Henschke, J. & Sosinska, A. (1998). *Radiation Atlas of Poland 1997*. Agencja Wydawnicza ARIES, Warszawa.

Kozlowski, S. (1990). Deposits of building and road stones. In: Osika, R. (ed.) *Geology of Poland. Vol. VI. Mineral deposits.* Wyd. Geol., Warszawa, 288-295.

ORTEC (2000). *Gamma Vision – 32 for M-1. Gamma-Ray Spectrum Analysis and MCA Emulator for Microsoft Windows 95, 98, and NT.* Software User's Manual. ORTEC Part No. 774780, Oak Ridge.

Van Schmus, W. R. (1995). Natural radioactivity of the crust and mantle. In: Ahrens, T. J. (ed.) *Global Earth Physics.* American Geophysical Union, Washington, 283-291.

SOURCES OF TENORM - INVENTORY OF PHOSPHATE, FERTILISERS AND ALUMINIUM INDUSTRY

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Abstract

I. Phosphate fertilizers industry

In Romania, there were built and commissioned in the period 1964-1978, 7 fertilizers plants based on H_2SO_4 and HNO_3 attack.

H_2SO_4 attack

The deposit with sub-products (phosphogypsum) from SC SOFRET SA *Bacau*

The material (phosphogypsum) resulted from H_2SO_4 attack of the imported phosphatic rocks has been deposited since 1978, close to the plant, which is located in the Eastern part of *Bacau* city.

In the samples resulted from the surface of the phosphogypsum deposit and also from drills until a depth of 16 m there were detected the following contents in

radioelements: U=15-21 ppm, Ra^{226}=0,45-0,87 Bq/g, Th=<3 ppm, K=<1%, gamma dose flow rate between 0,18-0,25 µSv/h.

Radon concentration at the pond surface (irregular areas) was of 4860 Bq/m^3 and for thoron was of 496 Bq/m^3.

B. HNO_3 attack

The tailing pond with sub-products from S.C. AZOMURES S.A. *Targu-Mures*

The tailing pond with technological water and calcium carbonate occupies a surface of about 33 ha, close to the plant, which is located in the Western part of *Targu-Mures* city.

The technological water from the tailing pond has a pH=1,45 and the contents in U=0,045 mg/l and Ra=1,4 Bq/l

The sub-product (calcium carbonate) contains 23 ppm U, 0,35 Bq/g Ra, 2 ppm Th and 0,2% K.

II. Aluminum industry

A. Alumina Plant from Oradea

In the western area of Oradea city there is the bauxite processing plant.

In the pond with red sludge resulted from alumina acquirement, the contents in radionuclides are mentioned below (Table 2):

Table 2

	ppm U	Bq/g Ra	ppm Th
Material of red colour	11	0,21	61
Material of dark colour	<10	0,137	70
Material of light colour	127	1,675	11

In air at the pond surface: Rn^{222}=21 Bq/m^3, thoron=1220 Bq/m^3.

In water from the red sludge pond: Rn^{222}=101 pCi/l, thoron = 0, Ra^{226}=0,023 Bq/l, pH=12,05.

B. Alumina Plant from Tulcea

Sub-product – red sludge: U=15 ppm; Ra^{226}=0,212; Th=62 ppm.

In water from pond: pH=12,2; Ra^{226}=0,026 Bq/l; U=0,010 mg/l.

Rn^{222} and thoron distribution in air at the red sludge pond surface: Rn^{222}=248 Bq/m^3, thoron=6270 Bq/m^3.

Introduction

For activities linked to uranium ore mining and processing – due to high content of U, Ra and other decays, the international and national organizations elaborated radioprotection norms concerning the admitted limits for personnel and public additional exposure.

Less attention was paid to population or workers exposure as a result of the utilization of some materials with naturally occurring radionuclides – NORs – but their radioactivity may not be ignored.

In these cases, the industrial processes can determine a concentration intensification of some radionuclides (U, Ra, K and Th) in the final products, in intermediary ones, in technological waters or residual materials.

As the potential additional exposure could result from such materials manipulation and also from residual utilization or evacuation, EC sustained a work program in this fields orientated to the following industrial activities:

- Coal based power production;
- Phosphatic ores processing;
- Aluminium production;
- Oil and gas production;
- Metal and titanic oxide processing;
- Metals smelting;
- Copper processing;
- Ceramics and zirconium industry;
- Building materials deposits;
- Radium and thorium natural radionuclides applications.

Many of the above categories haven't been considered as industries with a potential radiological impact on people or environment and they are not under a radiological control because they are not systemically monitored.

On that account, there are necessary studies to determine and inventory the additional natural irradiation sources from different geographical zones, as a result of the "technological activities", in order to assess and control the intervention level regulation in case of increase of additional natural irradiation of the population or workers.

Phosphate fertilizers industry

In Romania, there were built and commissioned in the period 1964-1978, 7 fertilizers plants based on H_2SO_4 and HNO_3 attack.

2.1. Wet Process

H_2SO_4 attack

The dihydrate wet process which is the base of all the phosphoric acid plants from Romania, is the process with the largest world spread all over the world due to its simpleness and especially due to working possibility with any phosphatic rock type whose content in P_2O_5 can vary between 29-39% P_2O_5.

Raw materials used at phosphoric acid manufacture are:

- phosphatic rocks with P_2O_5 content varying between 29 and 39% P_2O_5;
- concentrate sulfuric acid 94-98%.

This is by far the most important process discussed here and is based on the chemical reaction:

$$Ca_{10} (PO_4)_6F_2 + 10\ H_2\ SO_4 + 20\ H_2O \rightarrow 6\ H_3\ PO4 + 10\ CaSO_4{\cdot}2H_2O + 2HF$$

From this process, two products resulted:

- phosphoric acid (liquid phase) where more than 90% of Uranium from the rock is found;
- gypsum usually named phosphogypsum is the solid phase which may also carries 80% of the Ra^{226} initial existent in the phosphate rock. Phosphogypsum may also carry 5-20% of uranium from the rock.

Phosphoric acid obtained (50-52% P_2O_5) can be combined with ammonia to produce ammonium phosphate or can be combined with phosphorite in triple ratio to produce superphosphates.

From the phosphoric acid facilities results the following production waste :

- Solid waste – phosphogypsum
- Liquid waste – acid waters
- Gaseous waste – fluorine

For contamination prevention of the environment factors: water, air, soil, underground by one of the above-mentioned wastes, using specific technological measures, this difficulty can be forestalled.

Phosphogypsum - solid waste, resulted from the filtration stage can be evacuated from plant:

- Hydraulically, when it is collected together with chemically impure waters from plant, in a phosphogypsum recipient, where it is neutralized at the same time with the waters by $Ca(OH)_2$ 10% and after that, it is deposited by pumping in an impermeable settling tank, the decanted waters being recirculated in the plant.
- Mechanically, when it is evacuated from the plant, by means of a convey belt, on a waterproofed waste heap with ditches.

The chemically impure waters - are neutralized at the same time with phosphogypsum, evacuated in neutralization recipients, decanted and then evacuated in sewage.

The sub-products (phosphogypsum) deposit from S.C. MARWAY – FERTILCHIM S.A. *Năvodari.*

The sterile (phosphogypsum) has been deposited in three ponds located in the western part of the processing plant.

- Tailing pond A, on function from 1961, was decommissioned in 1975 and has a volume of 1.150.000 m^3, partially covered by spontaneous vegetation;
- Tailing pond B, was abandoned in 1996, in which the sterile was deposited beginning with 1975; it occupies a surface of 21 ha and has a height of 7-11 m;
- Tailing pond C, is operating since 1996 and occupies a surface of 10 ha.

The medium U, Ra, Th, and other elements contents from the collected samples are presented below (Fig. 1,2): U=15 ppm; Ra=0,48 Bq/gr; Th=<3 ppm; K=1,48%; Al_2O_3=0,4%; V=2 ppm; Sn=30 ppm; P_2O_5=0,57%; Pb=15 ppm; Cu=20 ppm; S=18%; ppc=21%.

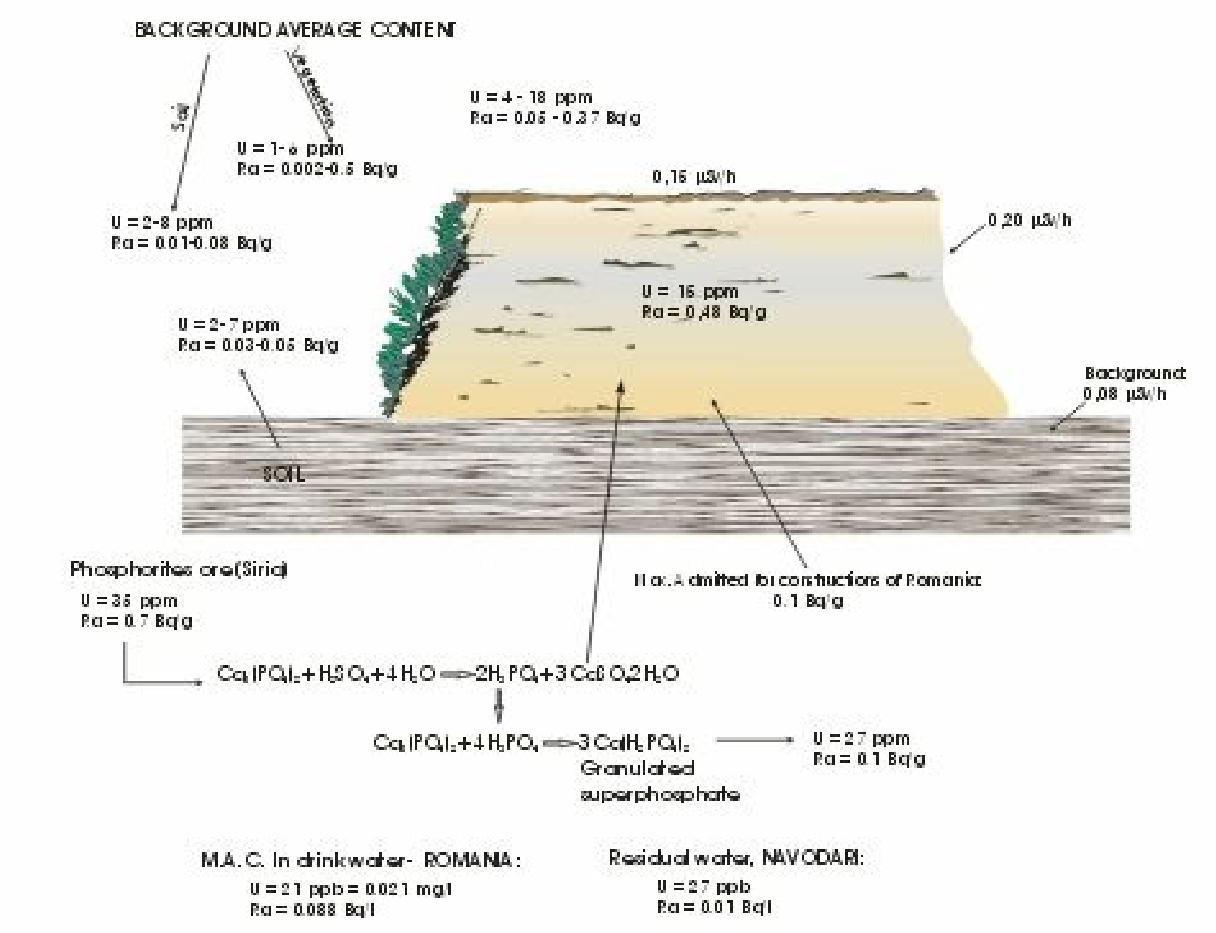

Fig. 1. Dump of phosphogypsum – Navodari

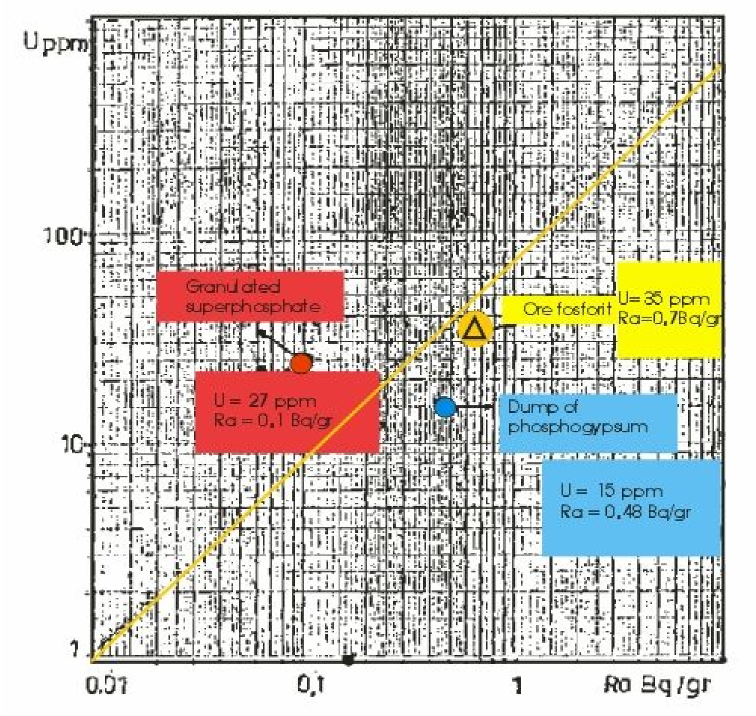

Fig. 2. The distribution of U and Ra in row material, phosphogypsumand granulated superphosphate

In the last years, the processed ore was phosphorite from Syria; it has the following composition: P_2O_5=30,2%; CaO=47%; SiO_2=3,2%; ΣTR_2O_3=0,3%; MgO=0,7%; Cl=0,07%; F= -; Na_2O=0,2%; K_2O=0,03%; Ra=0,7 Bq/gr; U=0,0035%; Zn=0,018%; Be=0,002%; Ba=0,03%; Pb=0,002%; Cu=0,003%.

In 35 years of plant functioning, the raw material was brought from Marocco, Algeria, Egypt, Indonesia, Tunisia, and Israel. This raw material has similar composition as concerns the fundamental elements P_2O_5, CaO, but with variations concerning the minor elements and especially the radioactive ones.

Gamma dose flow rate on the entire pond surface is between 0,18-0,22 μSv/h compared to a 0,08 μSv/h background value.

The technological water from pond C contains the following elements: Fe=7 mg/l; Ca=1000 mg/l; PS=0,4 mg/l; Cu=0,5 mg/l; Ra=0,01 Bq/l; Zn=0,7 mg/l; U=0,027 mg/l.

<u>The deposit with sub-products (phosphogypsum) from S.C. SOFRET S.A. *Bacau*</u>

The material (phosphogypsum) resulted from H_2SO_4 attack of the imported phosphatic rocks has been deposited since 1978, close to the plant, which is located in the Eastern part of *Bacău* city.

Phosphogypsum has been evacuated by a convey belt and occupies a surface of 28 ha. In the last year, the processed ore has been brought from Togo and has the following radio elements contents: U=117 ppm; Ra=1,300 Bq/gr; Th=27 ppm; K=1,5%.

In the ore deposit, gamma dose flow rate was between 0,5-1,3 μSv/h and the concentrations were: Rn=104 Bq/m^3 and ; Thoron= 346 Bq/m^3 .

In the KCl ore deposit imported from Russia, the concentrations are: Rn^{222}=22,2 Bq/m^3 and thoron=0 Bq/m^3.

The ore has a content of 57,08% K, 2 ppm U and 0,015 Bq/g Ra.

In the samples resulted from the surface of the phosphogypsum deposit and also from drills until a depth of 16 m there were detected the following contents in radioelements: U=15-21 ppm;Ra^{226}=0,45-0,87 Bq/gr; Th=<3 ppm; K=<1%; Gamma dose flow rate between 0,18-0,25 μSv/h.

Radon concentration at the pond surface (irregular areas) (Fig.4) was of 4860 Bq/m^3 and for thoron was of 496 Bq/m^3.

2.1.2. The sub-product from HNO_3 attack

The only manufacture waste is calcium carbonate at the calcium nitrate conversion stage. The product is easily filterable, very reactive in case is used as agricultural amendment.

The granulation is comprised between 40÷100 microns, the medium one being between 60÷80 microns.

The humidity is of max. 15% free water when it is sent to the waste heap.

The waste calcium carbonate quantity depends strictly on CaO content in the phosphatic rocks utilized at nitro phosphate producing. At a capacity of about 300 t

P_2O_5 100% / day in complex fertilizers, for the calculus medium rock about 700 t dry $CaCO_3$ / day, respectively 231000 t $CaCO_3$ / year.

The tailing pond with sub-products from S.C. AZOMURES S.A. *Targu-Mures*

The tailing pond with technological water and calcium carbonate occupies a surface of about 33 ha, close to the plant, which is located in the Western part of *Targu-Mures* city.

The raw material imported from Marocco and Kola has the following chemical composition:

	Marocco	Kola
P_2O_5	24,13%	34,23%
CaO	52,32%	45,7%
MgO	0,26%	0,5%
F	3,56%	3%
Na_2O	0,77%	0,3%
SiO_2	1,75%	10%
Al_2O_3	0,33%	4%
Fe_2O_3	0,5%	
U	131 ppm	11 ppm
Ra	1,51 Bq/g	0,125 Bq/g
K	0,07%	0,10%
Th	3 ppm	17 ppm

- the technological water from the tailing pond has a PH=1,45 and the contents in U=0,045 mg/l and Ra=1,4 Bq/l;
- the sub-product (calcium carbonate) contains 23 ppm U, 0,35 Bq/g Ra, 2 ppm Th and 0,2% K.

The radionuclides content in fertilizers varies depending on the chemical composition of the raw material used for their producing as well as on the attack process (Table 1, Fig. 3).

Table 1

Fertilizer	H_2SO_4 attack						HNO_3		
	BACAU			NAVODARI			TARGU-MURES		
	U ppm	Ra Bq/g	Th ppm	U ppm	Ra Bq/g	Th ppm	U ppm	Ra Bq/g	Th ppm
Ammonium nitrate	-	-	-	-	-	-	5	0,015	2
NPK	2	0,015	1	-	-	-	21	0,26	6
NP	5	0,079	38	-	-	-	29	0,36	4
Granulated super phosphate	-	-	-	27	0,1	3	-	-	-

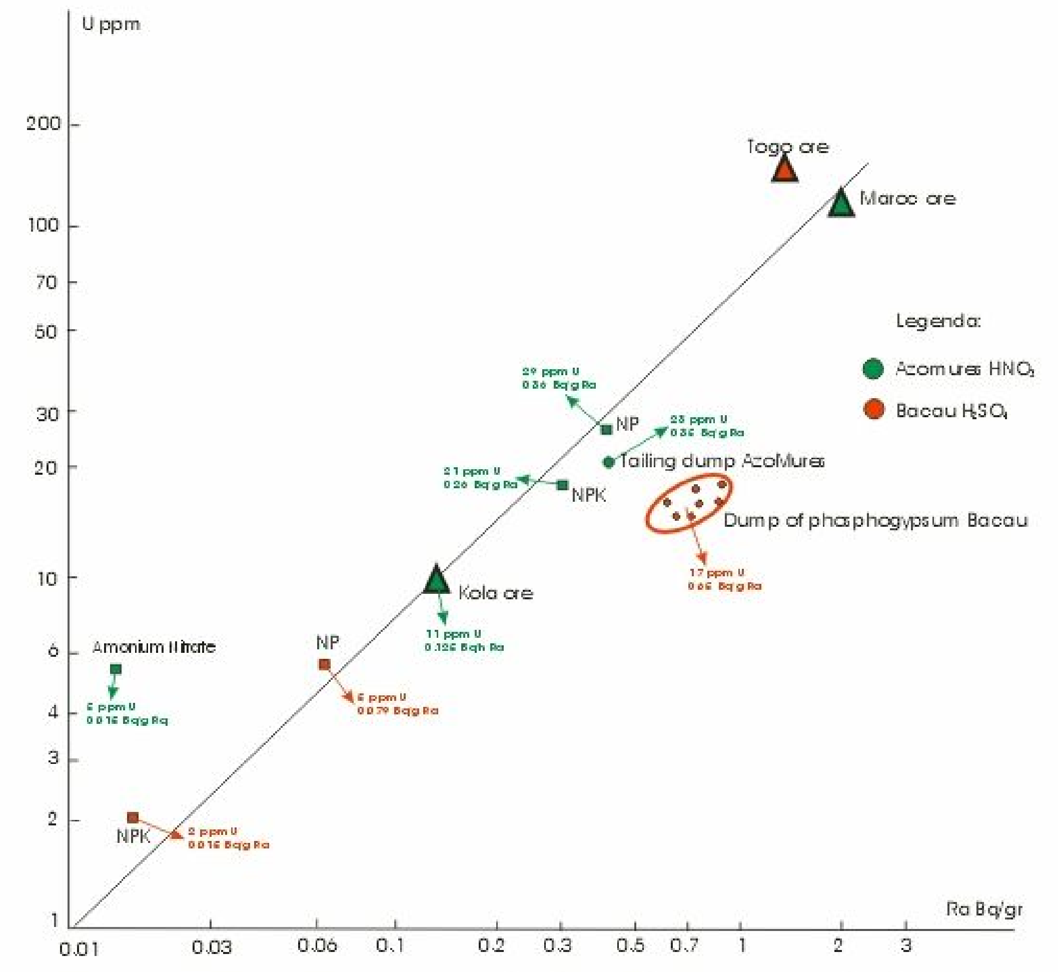

Fig.3. The distribution of U and Ra in row material phosphogypsum and phosphate fertilizers

3. Aluminium industries

3.1. Mining

Bauxite is the most important raw material for aluminium production, the last one being a mixture of aluminium hydroxides, with iron hydroxides and oxides (specular iron, goethite), with hydrated aluminium silicates, colloidal silica, titanic oxides and water.

The bauxite content varies in appreciable limits for the main components: Al_2O_3=40,75%; Fe_2O_4=2–37%; SiO_2=1-25%; TiO_2=1-5%; H_2O=8-28%.

The bauxite used in aluminium metallurgy has to contain over 45% Al_2O_3 in the ratio $Al_2O_3/SiO_2 = 3$.

In Romania, the exploitable bauxite concentrations are located in *Padurea Craiului* region. Their genesis was very much discussed. Till 1970 it was accepted the idea that the aluminium ore represents the lateritization products of aluminium rich clay impurities from the tithonic limestones in tropical climate conditions. These products have been concentrated in the karst relief of tithonic limestones and covered by Neocomian limestones. This conception, which was well accepted by many researchers from other countries, was gradually replaced with the conception that the initial material lateritic transformed even for bauxite located on limestones was constituted from andesite through their pyroclastic products.

The chemical composition of the exploited ore from *Rosia* zone, processed then at the *Dobresti* plant was the following: SiO_2=4,50%; Al_2O_3=55,00%; FeO=0,5%; Fe_2O_3=25,00%; TiO_2=3%; CaO=1%; ppc=11% .

Mineralogical components is:

- Kaolin	– 8%
- diaspore + boehmite	– 53,60%
- leptochlorite	– 0,63%
- hematite	– 24,8%

- Radionuclides distribution in the products obtained at the *Dobresti* processing plant is presented below:

	ppm U	Bq/gr Ra	ppm Th
Bauxite stock before grinding	12	0,162	30
Final product after washing	<10	0,062	31
Sterile	10	0,11	22
Material from *Dobresti* pond	<10	0,087	28
Ore from Gallery 2 *Rosia*	16	0,112	41

- Rn and Thoron distribution in water and air from *Rosia* mine:
  - Air from gallery :

    Rn^{222}=55 Bq/m^3

    Thoron=208 Bq/m^3
  - Mine water :

    Rn^{222}=4,36 pCi/l

    Thoron= 0 pCi/l

    U=0,0044mg/l

    Ra^{226}=0,018 Bq/l

- *Dobresti* bauxite processing plant:
  - Air from bauxite deposit:

    Rn^{222}=0 Bq/m^3

    Thoron=127 Bq/m^3
  - Water from bauxite washing:

    Rn^{222}=348 pCi/l

    U=0,010 mg/l

    Ra^{226}=0,04 Bq/l
  - Water from bauxite processing pond (*Dobresti*):

    Rn^{222}=107 pCi/l

    U=0,0010 mg/l

    Ra^{226}=0,006 Bq/l

    Thoron=o Bq/l

The processed ore from *Dobresti* plant used to be transported to alumina plant from *Oradea*. The activity has been suspended for 1 year.

Concerning the centers of alumina and aluminium manufacturing in Romania, Al_2O_3 alumina is produced in our country at *Oradea* from the bauxite exploited from *Padurea Craiului* Mountains and at *Tulcea* from import.

3.2. TENORM

Sub-product – red sludge.

3.2.1. Alumina Plant from Oradea

In the western area of Oradea city there is the bauxite processing plant.

In the pond with red sludge resulted from alumina acquirement (Fig. 4), the contents in radionuclides are mentioned below:

	ppm U	Bq/gr Ra	ppm Th
Material of red colour	11	0,21	61
Material of dark colour	<10	0,137	70
Material of light colour	127	1,675	11

- Rn^{222} and thoron distribution:
  - In air at the pond surface:

    Rn^{222}=21 Bq/m^3

    Thoron=1220 Bq/m^3
  - In water from the red sludge pond:

    Rn^{222}=101 pCi/l

    Thoron=0

    Ra^{226}=0,023 Bq/l

    pH=12,05

Fig. 4. The red sludge pond from bauxite processing Oradea

3.2.2. Alumina Plant from Tulcea (Fig. 5)

The raw material is from import. It results from:

	ppm U	Bq/gr Ra	ppm Th
Brazil Trombeta zone	40	1,5	21
Guineea Bissau Boke zone	17	0,27	27

Sub-product – red sludge:

U=15 ppm

Ra^{226}=0,212

Th=62 ppm

In water from pond:

pH=12,2

Ra^{226}=0,026 Bq/l

U=0,010 mg/l

- Rn^{222} and thoron distribution in air at the red sludge pond surface:

  Rn^{222}=248 Bq/m^3

  Thoron=6270 Bq/m^3

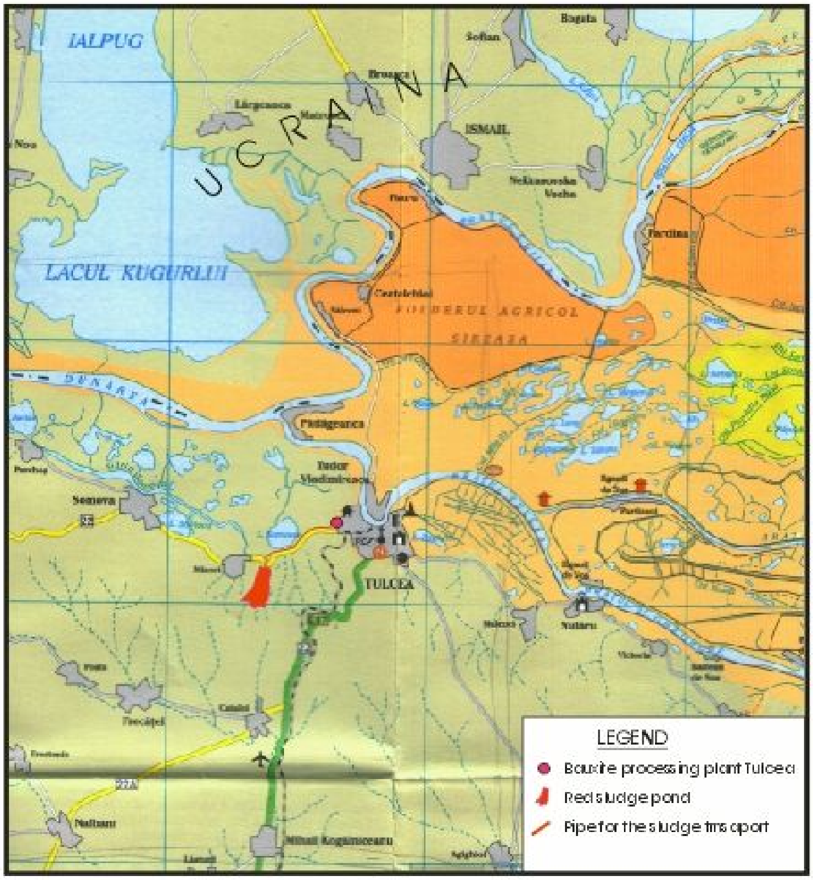

Fig. 5. Tulcea bauxite processing plant and the red sludge pond

4. Bibliography

1. Z.S. Altschuler, The bearing of Geochemistry on the recovery of Uranium and Rare Earths in phosphorites, 2nd IMPHOS Conf. Boston, 605, 1980.
2. F.J. Hurst, Recovery of Uranium from phosphates, IAEA – TECDOC – 533, 1989.

3. F. Bunuş, I.Miu, Uranium Recovery from Phosphates in Romania, IAEA – TECDOC – 823, 1995.
4. F. Bunuş, Gh.Filip, T.Coroianu, d.Filip – IAEA Tech. Committee Meeting Vienna, June, 1997.

RADON MEASUREMENTS AS A MONITORING POSSIBILITY FOR MINING SUBSIDENCE OCCURRENCES

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Abstract

The objective of the current research is to check whether or not subsurface radon concentrations can be related to mining and mining subsidence voids in order to allow the creation of a subsidence risk map. The chosen test site is located in the former Luxembourg mining basin. Under an overburden of 65 m thick limestone and marls iron ore bearing formations have been mined inbetween 1920 and 1950. Mining subsidence has progressively occurred for more than 50 years and is currently

going on. We report of intensive investigations on radon in soil measurements, distributed over parallel traverses. Radon concentrations plotted against sample spacing are very irregular showing inhomogenious subsoil. The maps of radon concentrations document these irregularities; furthermore it is possible to identify a trend corresponding to the main directions of the old mine roadways. The location of enhanced radon concentrations may point to a local increased subsidence risk, consecutive to a fractioning of the underground.

Introduction

The Luxembourg mining basin covers 3670 ha, located in the Southwest of the country (Fig. 1) and is the Northern continuation of the French ‘minette’ iron ore basin. The minette ore was extracted from the middle of the 19th century until 1981 at which time the last mine was closed. The extraction technique used in the underground mines was the room-and-pillar working where the ore is taken from a panel while pillars are kept in place temporarly in order to maintain the solidity of the roof. On the retreat, the pillars are gradually removed allowing the roof to collapse. In older mines, the geometry of the workings was often irregular and many pillars remained in place keeping the rate of extraction sometimes as low as 50 % (Storoni, 2001). Most of the undermined surface has been affected by ground subsidence during and after the mining period due to the fact that the thickness of the overburden, comprehending the overlaying sterile strata as well as the non exploited seams, reaches from a few meters at the outcrop of the ore layers to a maximum of 80 m along the French border.

Mines subsidence occurred and continues even more than 50 years after closure; the rate of surface collapse has nevertheless perceptibly diminished in the course of the last 30 years. The two types of ground subsidence that dominate in Luxembourg are crown holes and fissures. Crown holes mostly form on top of the wider mine voids, as they are the direct result of roof collapse between pillars. Sometimes they trace the pattern of the underlying mine. Individual subsidences may coalesce into depressions of different shapes. The depth of the resulting deformations vary from a few decimetres to as much as 8 to 10 m depending on the local bulk factor and the number and thickness of the extracted layers.

Throughout the mining period, subsidence related disturbances caused comparatively little damage as the mining area is scarcely occupied. Merely secondary roads, a few buildings, a municipal park, and a camping ground were damaged and had to be abandoned. New subsidence risks emerged at the end of the 20th century when notably undermined areas started to be considered apt to support urban facilities necessary for the development of the crowded industrial towns of the mining basin where about a third of the country's population lives. Time alone will not solve this risk problem because in areas prone to pillar failure and sinkhole development the subsidence risk may last for decades and even centuries after underground mining has stopped.

Experience has shown that the only safe management policy for mining areas prone to pillar failure under a thin overburden is to abandon them altogether or at least to ban any residential or industrial development from this land. On the other hand it cannot be excluded that sooner or later the development of the urban infrastructure will encroach on the mining land. Such a development will probably be delayed temporarily or it may be limited to restricted areas, so that managing the subsidence risks is not an urgent matter. On a few occasions though, positive expertise based on erroneous data had been forwarded, what shows that data on past mine workings and on former ground subsidence are not readily available. In fact, the greater part of the mining company records have disappeared by now or are in the hands of private collectors. The archives of the mining inspection authority are still available, but they offer only limited information. Recorded data on ground subsidence are extremely scarce, except for the first two decades of the mining period. Old air photographs may show ground subsidence on some occasions, but only if it was localised outside the forest and had not yet been reclaimed at the moment of the coverage. The only effective ways to document the type of subsidence and to determine the spatial aspects of the disturbances is a close and often tedious field investigation. Due to the poor information on the underground mine conditions and to the undeniable fact that under the prevailing conditions no zone of the mining area can be considered to be safe construction ground, new means of monitoring mines from the surface have to be investigated. Among different possible geophysical investigations we decided for a monitoring based on radon in soil air measurements.

2. Materials and methods

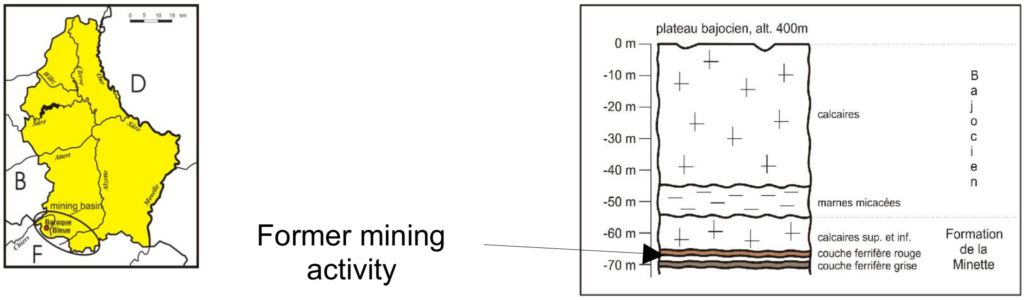

Fig. 1: a. Situation of the Luxembourg mining basin. b. The thickness and the nature of the overburden at the investigated site "Baraque Bleue".

The chosen test site called "Baraque Bleue" is located in a forested area on the plateau of the Luxembourg mining basin. Under an overburden of 65 m thick limestone and marls two iron layers have been mined between 1920 and 1950, in tunnels approximately 3 m high (Fig. 1). Along the western boundary a long surface fissure has developed and some 30 subsidence pits occurred over a period of several decades, the last developped in 1995 (Fig. 2).

The site was mainly chosen because it is situated in a forest area, it has a more or less uniform surface, the old mining maps still exist and further subsidence may be expected especially under the neighbouring busy road in the vicinity of which the most recent crown holes appeared.

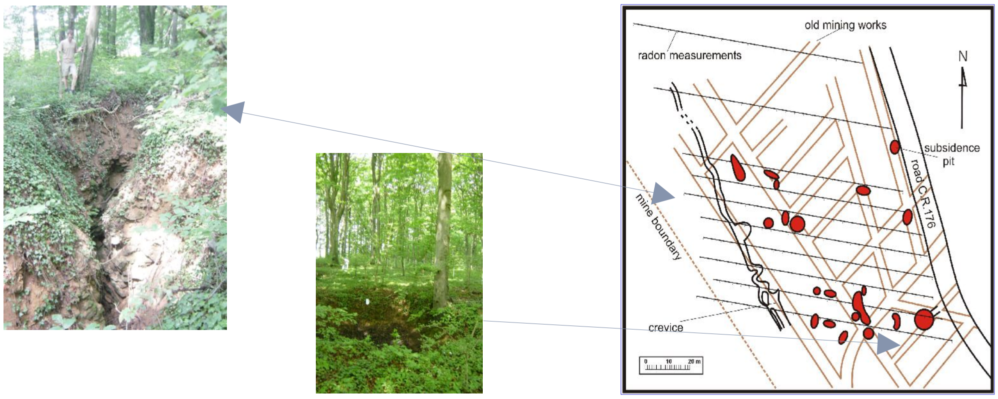

Fig. 2: The chosen test site “Baraque Bleue” is located in a forested area on the plateau of the former Luxembourg mining basin. Shown are examples of sinkhole occurrence over the old mine roadways and the location of the transects where soil-radon was measured. The locations of the underlying main galleries are approximate

The ease of radon to leave the site of production in the soil and rocks and the differences in the subsequent possibility to migrate and concentrate in underground voids, give the possibility to locate underground inhomogeneities by a survey based on radon soil measurements. Normally mining voids situated at a depth of 60 m have no influence on radon concentrations measured in one meter depth. But due to mining subsidence and the important brittleness of the rocks, fractures can develop and radon will be able to move up to the surface; as a consequence we expect locally increased radon concentrations. We report of an intensive investigation on radon in soil measurements, distributed over 10 parallel transects. Along a transect the spacing between the measurement points was 4 meter and 10 m between each transect. The last two transects had an offset of 30 m (Fig. 2).

The distribution of radon activity concentration in the subsurface gives very useful information and applications in many different domains. Variable concentrations often mean variable emanation and variable migration possibilities in a fractured medium. For indoor radon surveys, radon potential maps based on radon activity concentrations in soil gas are taken as an estimation of the geogenic radon potential (Kemski, 2001). In geology, geophysics and archaeology they give hints at underground inhomogeneities as faults, fractures, underground voids (Bornain 2003, Fischer 1992, Kies 1996).

A steel tube was hammered 1 m below the soil surface and a small void of several cm^3 was freed at the end of the rod. Compaction of the soil is small due to the small diameter of the rods. After venting a certain volume in order to purge the system, soil air samples were sucked into a syringe; 100 ml were introduced from the syringe into an evacuated Lucas cell. The measurements were performed after at least 3 hours in order to reach the equilibrium radon - fast radon decay products in the measuring cells.

For the present survey, all measurements were performed in a couple of days, thus minimizing an eventual seasonal variation; furthermore during the survey the weather conditions were dry and stable. The measurements were done without repetition, only for some holes soil gas was collected twice for a quality check.

Results and discussion

For the present study we were fortunate to have information from the old mining maps (Storoni, 2001). As the subsurface features we want to detect by the survey are elongated, the transects were taken across them, perpendicular to the underground directions of the main galleries.

Fig. 3 shows 7 of the resulting profiles displayed one above the other. It can be seen that the choice of the transect directions was a good one.

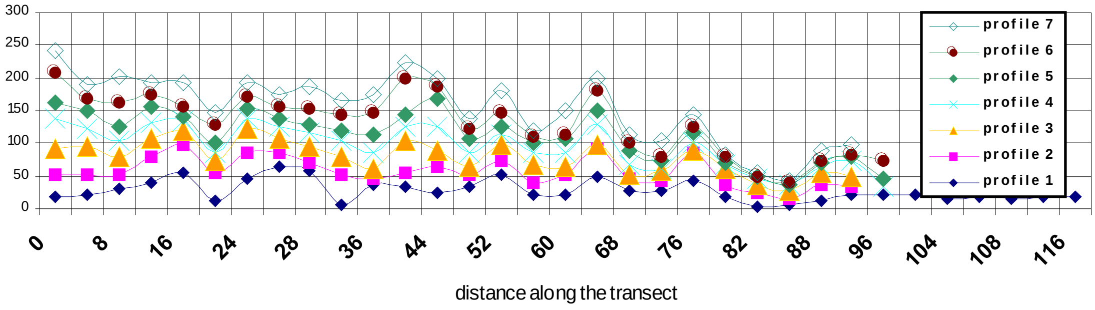

Fig. 3: Stacked profiles of the 7 parallel transects, inter-distance 10 m

As expected, the measured concentrations are log-normally distributed with the exception of some unusually low values (lower than 5 Bq/m^3) that have been omitted for the mapping. The median value is 25 kBq/m^3. Very low measured radon concentrations indicate an incorrect sampling or a disturbed soil; they introduce undesired lows during the mapping procedure (Fig 4).

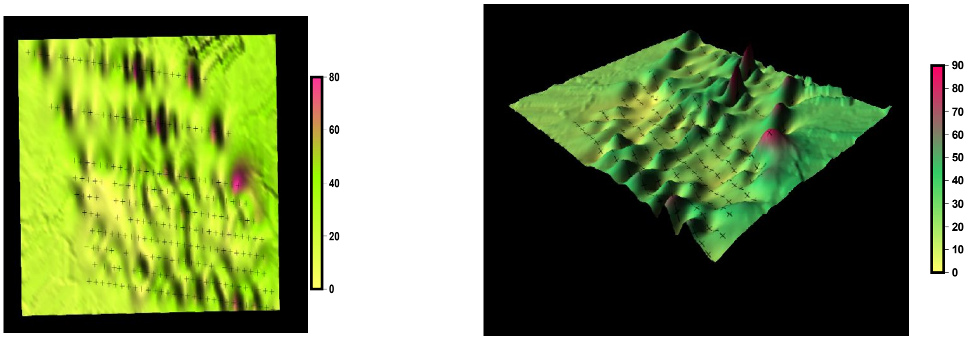

Fig. 4: Surfer maps show the distribution of the radon concentrations and the transects with the exact locations of the measuring points. Radon concentrations are given in kBq/m^3.

Radon concentrations plotted against sample spacing are very irregular documenting an inhomogeneous subsoil.

The maps of the radon concentrations (Fig.3, Fig 4) show these irregularities. Through the obtained maps, after kriging by the Surfer programme, it is possible to identify a trend from East to West, corresponding to the main direction of the underlying main tunnels. Locations of increased radon activity concentrations may present an increased risk for subsidence in the near future. An is alarming fact is that the points where radon concentrations are highest are situated close to a busy road.

Presently a study is initiated to double the investigations with gravity measurements. It will be interesting to compare the outcomong results.

Conclusion

The present study, based on the sole radon in subsoil measurements, shows a promising possibility to investigate on subsidence due to past mining activity. Locations with enhanced radon concentrations may imply an increased subsidence risk as a consequence to a fractioning of the underground. It is evident that a radon survey should be part of a vast investigation effort comprising other geophysical techniques.

References

Bornain S., A. Kies, M. Everaerts, 2003. Mise en evidence de failles à l'aide de mesures géomagnétiques et d'émanation radon dans la région de Stolzembourg. Geologica Belgica, 6/1-2 : 25-30.

Fischer H. J., 1992. Radonmessungen als Ergänzung des gängien Untersuchungs- und Bewertungsschemas zur Ausweisung von Deponiestandorten in geklüftetem, geringdurchlässigem Gestein, Schr. Angew. Geol. Karlsruhe, pp 1-206

Kemski J., Siehl A., Stegemann R., Valdivia-Manchego M., 2001. Mapping of geogenic radon potential in Germany, The Science of Total Environment, 272, pp 217-230

Kies A., Massen F., 1996. Investigation on radon concentration in different underground locations using different measuring devices, Int. Conf. on Technologically Enhanced Natural Radiation caused by Non-Uranium Mining, Central Mining Institute Kattowice, Szcyrk, Poland, pp. 365-374

Storoni A. 2001. Les formations d'afaissement minier dans le bassin ferrifère luxembourgeois, Publications du Service Géologique du Luxembourg, volume 30, pp 1-244

NATURALLY OCCURING RADIOACTIVE MATERIAL (NORM) ASSESSMENT OF OIL AND GAS PRODUCTION INSTALLATIONS IN NIGERIA

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Abstract

Naturally Occurring Radioactive Material (NORM) assessment was carried out at oil production platforms and gas processing units in Nigeria with the aim of establishing baseline levels and problem areas. The assessment consisted of external radiation measurements on production units, from the wellheads to the product outlets, sampling and gamma spectrometric analysis of scales and sludge from pig stations and of replaced pipes and vessels. The NORM levels on the installations and associated equipment ranged from 0.1 to 15μSv/h and γ spectrometric analysis indicate the presence of ^{226}Ra, ^{214}Bi and ^{214}Pb in the scales and sludge having

maximum concentration of 200 Bq/g. The levels may seem low but there is still the need to establish routine monitoring program for the Industry, which presently is non-existent.

INTRODUCTION

The presence of Naturally Occurring Radioactive Material (NORM) in the Earth crust is well known. ^{238}U, ^{235}U and ^{232}Th series are particularly important as they contain a number of radionuclides that are encountered in oil and gas products, produced water and in all sludge and scale deposits in sub and or surface production facilities.
The acronym NORM strictly speaking, refers to natural materials containing natural radionuclides in non-enhanced concentrations. The acronym TE-NORM, meaning Technologically Enhanced NORM has been introduced to distinguish NORM in the strict sense from materials with enhanced natural radioactivity as a result of human technology like oil and gas production.

NORM has developed from a little known issue to one that is receiving a large amount of global attention. The main reason for the increasing levels of concern are mostly from the large amount of NORM waste generated and the potential long term hazards resulting from the fact that NORM consists of long-lived radionuclides with relatively high radiotoxicities. Compared to artificial radioactive sources the activity levels found in NORM, even at elevated in oil and gas production and processing are not large. The potential hazard lies in the enormous quantity generated. In Nigeria there is now a renewed interest and focus on regulation of radioactivity including NORM (Elegba, 2002) and the oil industry is the most important sector of the economy with oil export accounting for 95% of Nigeria's export revenue.
A survey to carry an assessment of NORM in some oil and gas production installations in Nigeria was undertaken in this study. The Survey covered 10 manned offshore production platforms and two land terminals. The land terminals are an oil

separation production unit and a NGL production facility. The locations of the sites for this survey are not disclosed at the request of the site operators.

METHODOLOGY

An external gamma ray dose rate (μSv/h) survey was performed at the surface (1 cm) of well heads, production flow lines, separators, pumps, valves, storage tanks, and associated equipment at each location with a portable RADOS RDS-120 Universal survey meter manufactured by RADOS Technology OY, Finland. The instrument has a scintillation probe and in addition to two external probes, a GM probe and an alpha pancake probe. The measurement range is 0.05 μSv/h to 10 Sv/h with an automatic selection of the measurement range. Prior to each set of measurements at a location, a background reading was performed at positions, which are expected not to be influenced by NORM contamination. At each of the 12 locations the major production process line is monitored from the wellhead and pumps areas through the inlet pipes, separators, pumps to the outlet pipes and or storage tanks. Pig stations and replaced pipes on the platforms were also monitored and scales and sludge samples were taken. About 300 in-situ measurements were taken from the 12 installations and 20 samples of scales and sludge were taken for laboratory analysis. In the laboratory the samples were oven dried and later sealed in polyethylene vials for three weeks to allow equilibrium of ^{226}Ra with its decay products. The activity concentrations of the natural radionuclides were determined by low background gamma spectrometry using 12 h counting time with a HpGe detector having a resolution of 1.90 keV and relative efficiency of 20% at 1.33 MeV. The ^{226}Ra concentrations were derived from the weighted mean activities of the two photopeaks of ^{214}Pb (295.2 and 351.9 keV) and the three photopeaks of ^{214}Bi (609.3, 1120.3, 1764.5 keV).

RESULTS AND DISCUSSION

Approximately 300 measurements were performed at the surface of various components and equipment. The gamma dose rates ranged from 0.1 – 15 μSv/h with background value of 0.05 - 0.10 μSv/h. Most of the measured values are within the background values. In the gas plant the highest value of 0.14 μSv/h was measured at Pentane transfer pump area. This is not surprising since radon in NGL facility tends to be higher in pump and valves areas.

The highest measurements of 10 – 15 μSv/h were found at pig receiver stations and wellheads. These values are lower than most reported values elsewhere (Otto, 1989, Gray, 1993).

In assessing the occupational doses for workers at the 12 facilities, the most important factors are the dose rates and working time spent during normal activities and repairs. The exposure pathways are external exposure to gamma radiation, internal exposure to radon and radon daughters and inhalation of contaminated dust. The occupancy factors used to assess the occupational doses are 10 and 20 h/year for normal activities and repairs. The annual effective doses for the workers are not significant at less than 3 μSv/year for most of the locations. Even if the occupancy factors are doubled the doses to the workers are still relatively low.

With the low dose values for the monitored areas NORM appears not to be an immediate problem but still requires a monitoring program since mobilization of NORM increases with the lifetime of operations and the appearance of NORM also varies strongly between reservoirs, individual wells, installations and production conditions.

References

Elegba, S. B., 2002. Status of NORM in Nigeria: A new beginning. IAEA Technical meeting on Regulatory Approaches for the Control of Environmental Residues containing NORM, IAEA, Vienna, September 2002.

Gray, P. R., 1993. NORM contamination in the Petroleum Industry. JPT, 12-16.

Otto, G. H., 1989. A national survey on naturally occurring radioactive materials (NORM) in petroleum production and gas processing facilities. Report of the American Petroleum Institute, Dallas, Texas, USA.

RADIUM LEACHING FROM MINE DEPOSITS AND OTHER MATERIALS

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Abstract

Saline waters occurring in underground coal mines in Poland often contain natural radioactive isotopes, mainly ^{226}Ra from uranium series and ^{228}Ra from thorium series. Approximately 40% of total amount of radium remains underground in a form of radioactive deposits, but 225 MBq of ^{226}Ra and 400 MBq of ^{228}Ra are released daily to the rivers with mine effluents through surface settling ponds. Very peculiar situation is observed in coal mines, where as a result of precipitation of radium from radium-bearing waters radioactive deposits are formed. Sometimes natural radioactivity of such materials is very high, in case of scaling from coal mines radium concentration may reach 400 000 Bq/kg - similar activity as for 3% uranium ore. Usually such deposits can be found underground, but sometimes co-precipitation of radium and

barium takes place on the surface, in settling pond and in rivers. Therefore maintenance of solid and liquid waste with technologically enhanced natural radioactivity (TENORM) is a very important subject.

Lately another problem appeared – due to the decrease of the production of Polish coal industry and dismantling of several coal mines, also the ground reclamation should be done in their vicinity. But in several cases deposits in the ponds contain enhanced levels of radium concentration. Therefore laboratory tests were done to investigate a possibility of the re-entry of radium into groundwater or river waters from such deposits. Results show, that in case of insoluble barium and radium sulphates co-precipitated out from waters type A, re-entry ratio is very small. Different situation can be observed in case of radium, adsorbed on bottom sediments from waters type B, because re-entry ratio is much higher. This phenomenon seems to be important and significant to predict the pollution of the adjacent areas of the settling ponds in the future. Similar situation can be observed for other materials with enhanced radium content, for instance phosphogypsum. Therefore further study of radium leaching from different solid materials is necessary.

Introduction

Saline waters from underground coal mines in Poland often contain natural radioactive isotopes, mainly ^{226}Ra from the uranium decay series and ^{228}Ra from the thorium series. Approximately 40% of the total amount of radium remains underground as radioactive deposits, but significant quantities of radium isotopes is released daily into the settling ponds and rivers along with the other mine effluents from all Polish coal mines. Technical measures such as inducing the precipitation of radium in gobs, decreasing the amount of meteoric inflow water into underground workings etc., have been undertaken in several coal mines, and as a result of these measures the total amount of radium released to the surface waters has diminished by about 60% during the last 5-6 years.

Investigation by Tomza and Lebecka [1981] showed that concentration of radium in water is correlated with its salinity. As the salinity of mine waters usually increases with depth, waters with higher radium concentration occur in deeper levels. Two different types of radium-bearing water were found in coal mines [Skubacz et al., 1990]. One type (type A) contains high concentrations of radium and barium, but no sulphate ions, whilst the other (type B) has very low barium but high radium and sulphate. From type waters radium is easily co-precipitated with barium sulphate when mixed with other natural waters containing sulphate ions. For radium-bearing type B waters, there is no co-precipitant for radium, therefore precipitation does not occur. Further investigation [Lebecka et al., 1993] showed that radium bearing waters released from coal mines sometimes cause widespread contamination of both small and larger rivers in their vicinity. This contamination is caused by radium being present in ionic form in water as well as in suspended matter. Highly radioactive deposits are formed by co-precipitation of barium and radium as sulphates from radium-bearing type A waters [Tomza & Lebecka, 1981]. This process results in reduction of the total activity released into rivers because part of radium remains in the underground mine workings. Precipitation of barium and radium sulphates in underground mine workings takes place either spontaneously or as a result of applied treatment procedures which aim to reduce the radium concentration in waste waters below the permitted level.

The presence of barium in waters is the most important factor for the further behaviour of radium isotopes in mine galleries or on the surface. From waters type A radium and barium always co-precipitate as sulphates, when such waters are mixed with any water, containing sulphate ions. As the result of the precipitation of barium sulphate, deposits with highly enhanced radium concentrations, which may sometimes reach 400 kBq/kg, are formed [Lebecka et al, 1986]. In comparison, average radium content in soil is equal 25 Bq/kg [UNSCEAR, 1982]. In case of another type of radium-bearing waters (type B), no precipitation occurs due to the lack of the barium carrier. From such waters radium is removed in a slow process of sorption on bottom sediments in gauntons in underground galleries or on the surface in the settling ponds and rivers. In this case the increase of radium content in sediments is much lower as for waters type A. But we can observe enhanced concentration of radium isotopes in river waters or in bottom sediments on a long distance downstream from the discharge points [Michalik et al., 1999].

Nowadays a new problem arises – as a result of the decrease of the coal production in Poland several collieries were closed. In their settling ponds thousands of tonnes of bottom sediments with enhanced natural radioactivity remain. Radium from such deposits may be leached as a result of groundwater impact and may cause the contamination of the natural environment in the vicinity of abandoned mines. The study of that problem must be performed carefully.

The scope of investigations

The scope of investigations was focused on radium leaching from different types of mine deposits but additionally experiments with phosphogypsum were carried out to compare results with other scientists.

I. Firstly, a technique of radium leaching from solid materials has been developed during previous experiments [Chalupnik, 2000].
II. Appropriate methods have been chosen to determine concentration of radium isotopes in solid phase (gamma spectrometry) and in the solutions (liquid scintillation counting).
III. Analysis of obtained results has been done to enable prediction of the possibility of groundwater contamination in the vicinity of abandoned settling ponds.
IV. Additionally, a study of radium leaching from Spanish phosphogypsum has been performed to compare results of experiments with results of Spanish colleagues. One of the reasons was to check if results were depended of leaching technique.

3. Results of radium leaching

3.1. Measurements of radium concentration in solid phase

Solid samples were analysed for presence of radio-isotopes from the uranium and thorium decay series and ^{40}K. For these measurements a gamma spectrometry system was used - it comprises an HPGe detector (45%, PGT), multichannel analyser, built in the computer and the GENIE-2000 software for spectra analyses (CANBERRA). This instrumentation enables measurements of ^{226}Ra concentration (as low as 1 Bq/kg), ^{228}Ra and ^{210}Pb, ^{40}K and other natural and artificial isotopes [Lebecka et al., 1996] on the similar levels.

Different types of bottom sediments have been used in leaching experiments as well as phosphogypsum samples. Results of gamma spectrometic measurements are shown in table 1.

Table 1. Natural radionuclides in solid samples – concentrations in Bq/kg.

No.	Type of the sample	Ra-226 [Bq/kg]	Ra-228 [Bq/kg]	Pb-210 [Bq/kg]
1.	Type B bottom sediment from abandoned pond, mine R	1810±90	980±50	140±30
2.	Type B bottom sediment from abandoned pond, mine P	5900±300	9950±500	n.o.
3.	Spanish phosphogypsum	680±40	18±3	980±90

3.2. Leaching technique and measurements of radium in the solution

For leaching experiment 50 grams of dried solid sample has been used. Such amount of sample was mixed with 0.5 dm^3 of the solution (deionised water or other solvent). Firstly, the mixture was continuously stirred on magnetic stirrer for 1 hour and later left in the contact for a chosen time (from1 hour up to 7 days). Finally, after the filtration of the sample radium isotopes has been analysed and measured with the application of liquid scintillation spectrometry (LSC).

Radioactivity of waters from coal mines is mostly from radium isotopes - ^{226}Ra from the uranium series and ^{228}Ra from the thorium. A method of chemical separation of radium, developed by Goldin [Goldin, 1961], has been modified for liquid scintillation counting [Chalupnik & Lebecka, 1990; Chalupnik & Lebecka, 1993]. In this method, radium is co-precipitated with barium in form of sulphates and this precipitate is mixed with liquid gelling scintillator. The prepared samples were measured by a low background liquid scintillation spectrometer (QUANTULUS, Wallac Oy, Finland). This counter has alpha/beta separation with an anti-coincidence shield, which enables measurements of ^{226}Ra concentration above 3 Bq/m^3 with simultaneous measurements of ^{228}Ra (LLD = 30 Bq/m^3).

Deionised water has been applied as the basic solvent due to its very low ionic strength. Therefore this solvent should leach only this fraction of radium atom, which is loosely bond to the surface of sediment grains. It's a simulation of leaching caused by rain water. We predict elevated salinity of groundwater near settling ponds, therefore in some cases the solvent has been prepared from deionised water and sodium chloride NaCl (10 g per litre) with admixtures of potassium sulphate or carbonate (K_2SO_4 or K_2CO_3 - 2 g/l), barium or strontium chlorides ($BaCl_2$, $SrCl_2$ -1 g/l). We wanted to simulate leaching of radium by solutions with elevated mineralization and different chemical composition. Different admixtures have been used:

- to simulate presence of sulphate ions, which should decrease the radium leaching potassium sulphate was used;
- to simulate presence of carbonates in water, as radium carbonate is soluble potassium carbonate has been applied;
- to increase radium leaching and further possibility of co-precipitation of radium - barium chloride was added;
- strontium chloride was used to check its influence on the rate of radium leaching from deposits.

One of the important conclusions from measurements of radium content in deposits is following. To the settling pond of mine R waters with very low radium content has been discharged. The maximum concentration of ^{226}Ra never exceeded the value 0.15 kBq/m^3 [Chalupnik, 2002]. Despite this fact, radium concentration (^{226}Ra) in bottom sediments was 1.7-2.5 kBq/kg, while ^{228}Ra concentration was up to 1.5 kBq/kg. This is a confirmation of the fact, how important is radium adsorption on bottom sediments and other solid materials in settling ponds. After a certain time, radium content in solid phase may be high, also when radium concentration in water was low. Such phenomenon seems to be crucial in waterworks [Schoenhofer, 2001], especially in cases, when underground waters are treated.

3.3. Leaching of radium from deposits from mine R settling pond

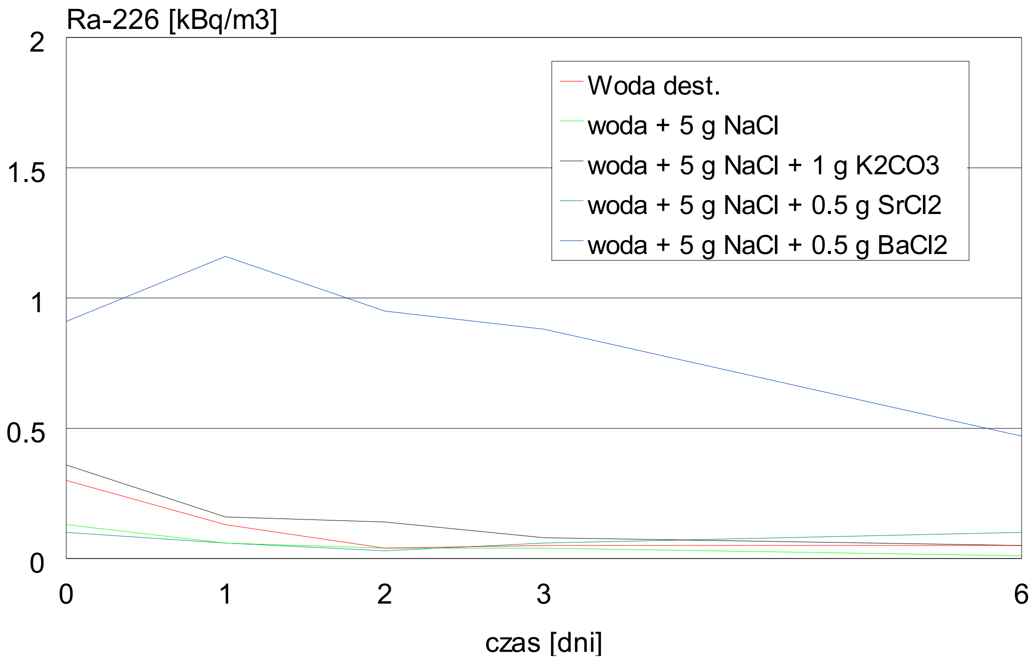
Samples of bottom sediments were taken from the settling pond during preparations to the ground reclamation of the area. Settling pond was located on the old pile of waste rocks, constructed from concrete blocks, connected and sealed against leaking. The thickness of the sediment's layer was of about 40 cm, while the surface of the pond was ca. 2000 m^2. The ground reclamation technique was following – the sediments have been covered by a thick layer of the waste rocks (of about 5 -7 meters). On the flat surface of the waste rocks, soil has been transferred from other places and finally trees and grass have been planted. Such method of ground reclamation was proposed by experts from Central Mining Institute.

In the sediment sample from the pond radium ^{226}Ra concentration was 1800 Bq/kg, while concentration of ^{228}Ra was close to 1000 Bq/kg. These sediments were relatively young (less than 2 years), as the ^{210}Pb concentration was equal 140 Bq/kg only.

After drying of sediments, 50 g samples were mixed with different solvents to calculate leaching coefficients from solid to liquid phase. Different solvent have been used, not only deionised water but also solutions of sodium chloride with admixtures of potassium carbonates or sulphates, barium chloride or strontium chloride.

Results of radium measurements in liquid phase after experiments are shown in fig. 1. Concentrations of ^{226}Ra are plotted in the function of the contact time.

Rys 1. Wymywanie radu z osadu KWK Rymer



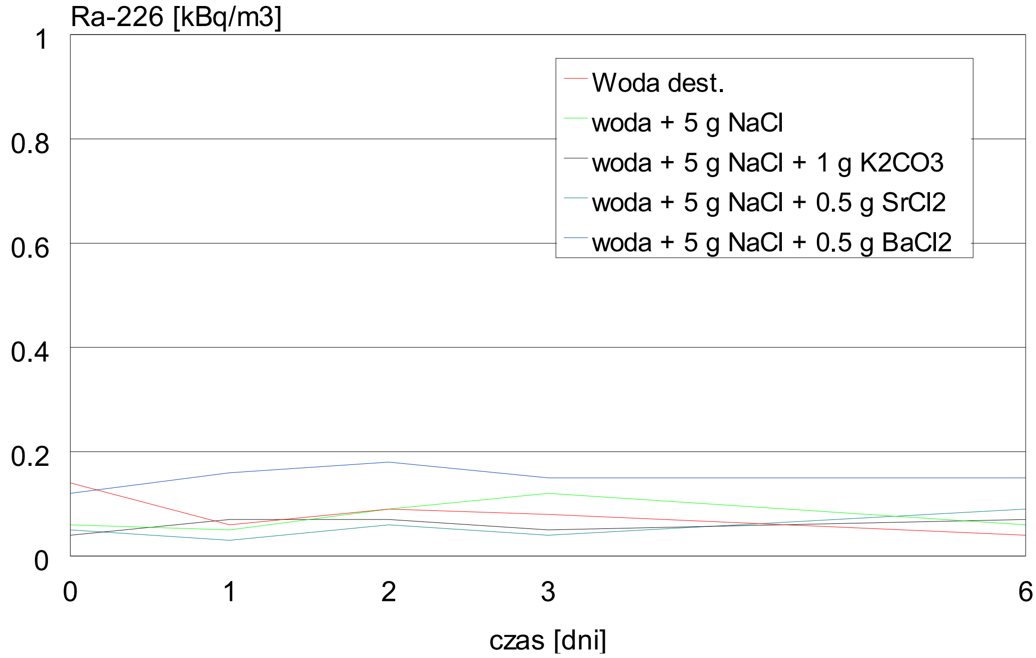
Samples of sediments contained approximately 90 Bq of ^{226}Ra and 50 Bq of ^{228}Ra. It can be seen on the picture, that fraction of leached-out radium was of about 0.6 Bq for ^{226}Ra (and 0.4 Bq for ^{228}Ra), when barium chloride solvent has been used. In case of potassium carbonate solvent only 0.2 Bq of ^{226}Ra and 0.2 Bq of ^{228}Ra were transferred from solid into liquid phase. The calculation of leaching coefficients gives following results – 0.6% of ^{226}Ra and 0.8% of ^{228}Ra have been leached into the barium chloride solvent and respectively 0.2% of ^{226}Ra and 0.4% of ^{228}Ra into carbonate solvent. For deionised water values of leaching coefficients were lower - 0.15% for ^{226}Ra and 0.3% for ^{228}Ra. It must be taken into considerations, that uncertainties for ^{228}Ra coefficients were rather high (at least 25%), even for maximum value. In case of ^{226}Ra uncertainties were lower – approximately 10%.

One important conclusion is that strontium presence doesn't influence the leaching of radium from deposits, opposite to barium. Chemical properties if strontium seems to be closer to properties of calcium, therefore strontium concentrations in mine waters shouldn't be correlated with radium concentrations.

3.4. Leaching of radium from deposits from mine P settling pond

In another series of experiments the bottom sediment from mine P has been used. Sediment sample has been taken from the abandoned settling pond 1.5 years after the release of water from the pond. During this time bottom sediments were exposed to the atmospheric precipitation and one of the aims of our investigations was to check if any changes of leaching coefficient can be seen. Sample was taken from the place, where highest values of radon exhalation factor have been measured. Moreover, in the same place samples of bottom sediments have been taken a year ago. It gives us the opportunity to check the changes of radium availability in the upper layer of sediments. In this part of the pond the total thickness of deposits was of about 1 meter. Despite the fact, that deposits were soaked with water almost entirely, radon exhalation was extremely high, up to 350 mBq/(m^2*s). Radon exhalation may be an important source of radiation hazard in such areas, therefore reclamation techniques of abandoned settling ponds must be chosen properly. Results of radium leaching from bottom sediments of mine P settling pond are shown in fig.2.

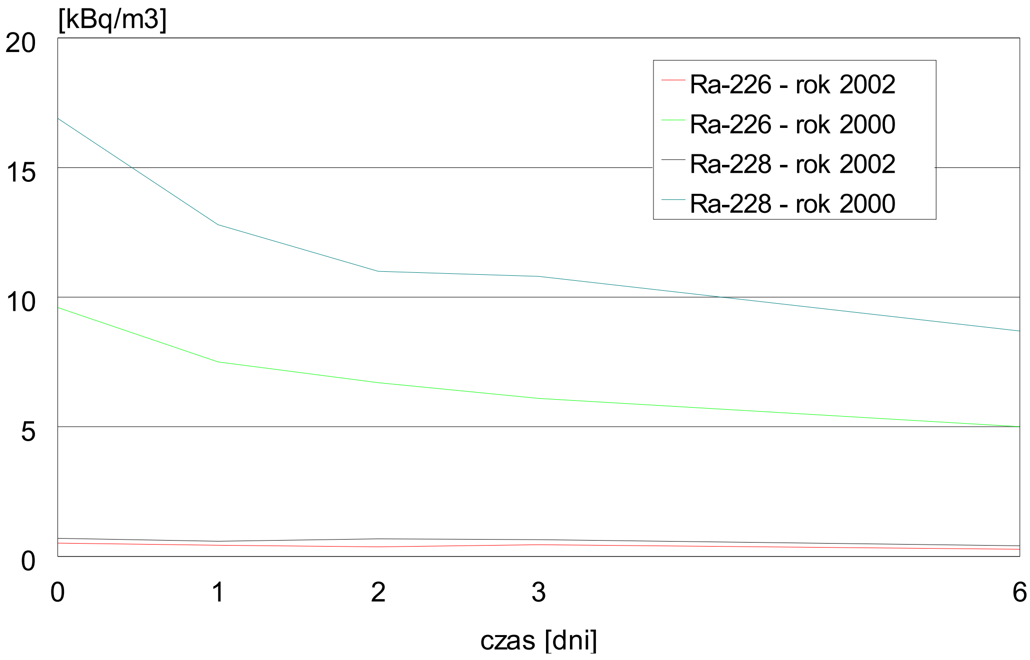
Rys 3. Wymywanie radu z osadu zbiornika Bojszowy



Sediments from settling pond P contained 29 Bq of ^{226}Ra and 50 Bq of ^{228}Ra in 50g sample. Fig.2 contains collected results of experiments, performed with different solvents. Maximum values of radium content in the solutions after leaching experiments were as follows: 0.1 Bq for ^{226}Ra and 0.15 Bq for ^{228}Ra. Calculation of leaching coefficient has been done and maximum values were at level 0.3% for both radium isotopes. No significant differences have been observed between particular solvent, except slightly higher concentrations in barium chloride solvent. Similar effect has been found for such type of deposits during earlier investigations [Chałupnik, 2002].

These results were surprisingly low in comparison with previous results of radium leaching from sediments, taken from the same pond and site two years earlier. Previous investigations showed leaching factor values up to 10%. A comparison of these results is shown in fig. 3.

Rys 5. Porownanie wymywalnosci radu z osadow osadnika Bojszowy



We suppose, that such significant differences may be due to two possible reasons. One of the reasons is dry-up of the sediments and chemical processes, in which radium may be involved during relatively long time. Another possibility is that bulk part of radium was already leached by rain waters into deeper layers of sediments, while samples were taken from the surface. Two conclusions can be drawn from that comparison. Firstly, bottom sediments in settling ponds must be isolated from groundwater and meteoric waters. The transfer of radium into liquid phase from dry deposits is very low therefore possibility of the groundwater contamination is also low. In such case the contamination of adjacent areas should be meaningless.

On the other hand, radium leaching by meteoric waters is sometimes significant, especially in case, when deposits are not covered for a long time. Therefore deposits with enhanced radium concentrations shouldn't be disposed on the surface waste piles, where seepage of rain waters might be an important source of contamination of surface waters.

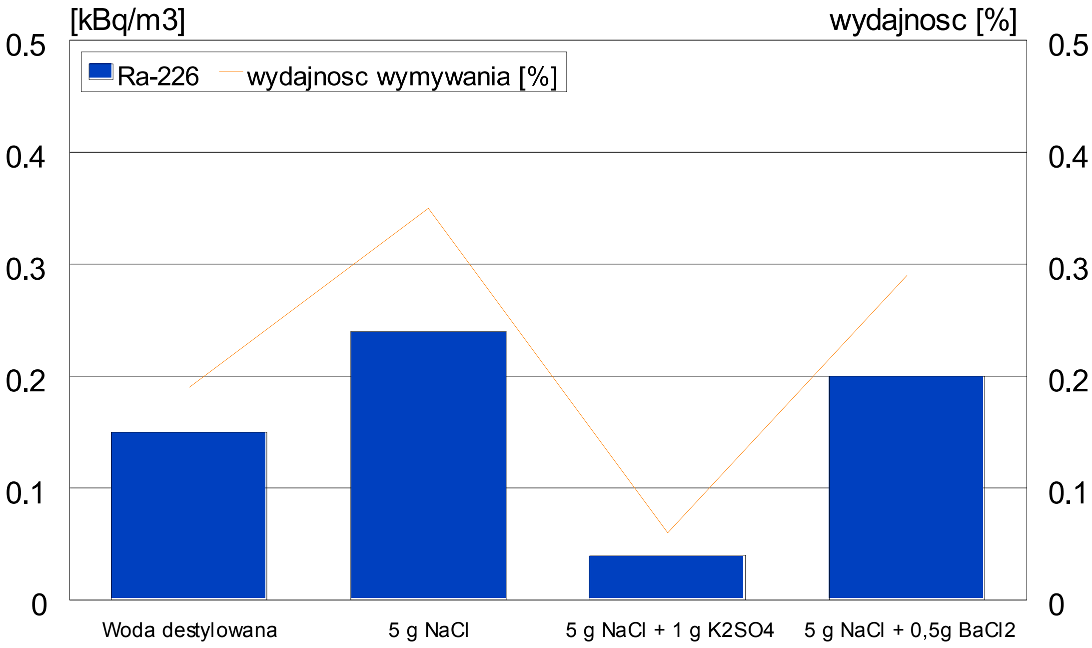
4. Comparison of the technique with other institutes

In last years investigations of radium leaching from different materials became more and more important issue. Different institutions considered this phenomenon as a significant source of the pollution in the vicinity of settling pond and waste disposal tips. For instance, during NRE VII Conference several presentations were focused on this subject. But results of different experiments varied significantly for similar samples, probably due to different leaching techniques. To check such possibility a comparison measurements have been started in the Central Mining Institute

At first, a comparison has been proposed for the team from Huelva University, Spain [Aguado, 2001]. During investigations, made in this centre, it has been found, that leaching factors for phosphogypsum into water phase were of about 1%. Leaching time varied from 7 to 14 days. Concentration of radium has been measured with application of liquid scintillation technique.

Small sample of phosphogypsum (200 grams) has been analysed in the Central Mining Institute Firstly gamma spectrometric analysis has been done (see table 1). Later leaching experiments were performed, accordingly with the technique, used routinely in our laboratory. The only difference was smaller amount of the solid sample (25 g instead of 50 g) mixed with the solvent. Results of experiments are shown in fig. 4.

Rys.10. Wymywanie radu z fosfogipsow hiszpanskich



Calculations of leaching coefficients give a wide range of values, depends on the solution, For instance, in case of barium chloride solution, the coefficient is lowest, only 0.04% and for deionised water - 0.19 %,. Highest values have been found for sulphate solvent (0.29%) and for solution with enhanced salinity 0.35 %. Obtained results are in a good agreement with results of Spanish colleagues.

The most significant difference between leaching processes from mine sediments and phosphogypsum seems to be different influence of barium presence in the solvent. In case of bottom sediments from settling pond presence of barium ions in the solution is leading to the increase of radium leaching. For phosphogypsum opposite situation is observed. This problem can be explained rather easily – phosphogypsum is partly soluble and in water sulphate ions appear as a result of this process. It leads to the co-precipitation of barium and radium as sulphates, i.e. secondary removal of radium from liquid phase and decrease of effective leaching coefficient. On the other hand, the admixture of potassium sulphate has no effect as well, as sulphate ions are already in the solution.

To compare results for different types of phosphogypsum further experiments with phosphogypsum samples form Greece, Czech Republic and Poland has been started.

Conclusions

Results of investigations confirmed our preliminary assessments, that leaching of radium from mine sediments, formed from B type waters, may be an important source of groundwater contamination in the vicinity of settling ponds. Therefore special methods of ground reclamation should be applied in such areas to decrease a potential pollution of the natural environment. Main issues are mitigation of groundwater flow through sediments and designing of an appropriate monitoring system. It will increase costs of ground reclamation.

Contrary for A type water sediments, radium concentrations are often much higher but leaching effects are extremely low. Ground reclamation of settling ponds with such sediments should be cheaper and safer for the environment and population of adjacent lands. Unfortunately, scarce data are available, concerning long term fate of radionuclides in such deposits. Therefore further investigations are necessary.

Sediments with enhanced radium content can be formed as results of long term release of waters with low radium content or treatment of groundwater in waterworks. All sediments from such settling ponds or filters should be examined for the presence of radionuclides. Appropriate methods of disposal must be applied to avoid contamination of the natural environment.

Comparison of results of leaching experiments shows, that a kind of standard method should be developed for this purpose, despite the fact that different techniques in different laboratories have given comparable results. Further comparisons and unification of the methods are necessary.

Our investigations show, that the process of radium leaching from mine deposits into groundwater or surface waters in not a marginal problem for the environmental protection and requires more attention in the future.

References

1. Sałdan M. - Metalogeneza uranu w utworach karbońskich GZW - Biuletyn Instytutu Geologicznego, Vol.5, Warszawa, 1965.
2. Tomza I., Lebecka J., Radium Bearing Waters in Coal Mines. Proc of Int. Conf. on Radiation Hazard in Mining. Golden, Colorado, USA, 1981.
3. LEBECKA J., i wsp - *Influence of Mining Activity on Distribution of Radium in the Natural Environment* - Proc. of 4th Working Meeting Isotopes in Nature, Leipzig, (1987).
4. Skubacz K., Lebecka J., Chalupnik S., Wysocka M., - Possible changes in radiation background of the natural environment caused by coal mines activity, International Symposium on Nuclear Techniques in Exploration and exploitation of Energy and Mineral Resources, IAEA-SM-308, Vienna, June 1990.
5. Ministerstwo Górnictwa i Energetyki - Wytyczne kontroli skażeń promieniotwórczych środowiska naturalnego powodowanych przez kopalnie węgla kamiennego - Katowice 1986.
6 Lebecka J. i wsp. - Skażenia promieniotwórcze na Górnym Śląsku powodowane przez wody kopalniane i wytrącające się z nich osady -Wiadomości Górnicze, 6/91, Katowice 1991.
7. Wysocka M. et al., Survey of Radon in Houses in an Area Strongly Affected by Mining activity, Gas Geochemistry, pp 481-487, 1995.

8. M. Wysocka i wsp. - Określenie ładunków substancji promieniotwórczych odprowadzanych przez kopalnie węgla kamiennego i rud miedzi do środowiska naturalnego - dokumentacja GIG w ramach grantu celowego KBN *STRATEGIA I DZIAŁANIA OGRANICZAJĄCE ZASOLENIE WÓD,* Katowice 1995.

9. Wysocka M., Lebecka J., Chalupnik S., (1997) – Ocena oddziaływania na środowisko naturalne wód radowych w sąsiedztwie zbiornika Bojszowy – *Raport dla Komitetu Badań Naukowych, GIG, Katowice, 1997*.

10. Michalik B., i wsp. 1999 - CONTAMINATION OF SETTLING PONDS OF COAL MINES CAUSED BY NATURAL RADIONUCLIDES, II International Symposium on Technologically Enhanced Natural Radiation, September 1999, Rio de Janeiro (w druku).

11. Lebecka J., Łukasik B., Chałupnik S., Purification of Saline Waters from Coal Mines from Radium and Barium, Int. Mine Water Congress, Nottingham, (1994).

12. Chalupnik S., 1999, Purification of mine water from radium - II International Symposium on Technologically Enhanced Natural Radiation, September 1999, Rio de Janeiro, (w druku).

13. Rajaretnam G., Spitz, H.B. – Effect of Leachability on Environmental Risk Assessment for Naturally Occurring Radioactivity Materials in Petroleum Oil Fields – Health Physics, 78 (2), 2000.

14. T. Wardaszko, Z. Pietrzak-Flis, I. Radwan - Occurrence of radium ^{226}Ra in Polish rivers and in bottom sediments in connection with mining activity in Upper Silesia – International Conference "Technologically Enhanced Natural Radioactivity, TENR'96, Szczyrk, 1996.

15. CHAŁUPNIK S., WYSOCKA M., *Wstępne wyniki oczyszczania wód dołowych z radu w KWK Piast, efekty I etapu wdrożenia*, Dokumentacja GIG, Katowice, 1999.

16. Chałupnik S., Lebecka J., „Determination of ^{226}Ra, ^{228}Ra and Ra-224 in water and aqueous solutions". International Conference on Advances Liquid Scintillation Spectrometry, Vienna 1992, Radiocarbon 1993.

17. Lebecka J., Skubacz K., Chałupnik S., Michalik B., „Methods of Monitoring of Radiation Exposure Used in Polish Coal Mines". Nukleonika 38, No4,137-154,1993.

18. Technical Report "The environmental behaviour of radium", IAEA, Vienna, STI/DOC/10/310, 1990.

19. Michałek-Piernik B., Pluta I., Arimoto R. – Wtórne skażenie barem wód odprowadzanych z KWK Silesia do środowiska, Materiały Konferencji „Współczesne problemy ochrony środowiska w górnictwie", Krynica 1994.

20. Skubacz K., i wsp.., 1993 – Ocena wielkości skażeń środowiska powodowanych przez zrzut wód radowych do Potoku Goławieckiego – Wiadomości Górnicze 5/93, Katowice.

21. Wiegand J., Feige S., – Leaching of radium recoil atoms from rock body - II International Symposium on Technologically Enhanced Natural Radiation, September 1999, Rio de Janeiro, IAEA-TCDOC-1271, Vienna 2002.

22. Aguado J., Bolivar, J.P., San-Miguel, E.G. – Ra and U isotopes determination in phosphogypsum leachates by alpha particle spectrometry - – Natural Radiation Environment Conference, NRE-VII, Rodos, 2002.

23. Koukouliou V., - Investigations of the Restoration of an Area Contaminated as a result of an abandoned Phosphate Fertiliser Industry – Natural Radiation Environment Conference, NRE-VII, Rodos, 2002.

24. Ghose, S. – The release of radium from scales, produced in the North Sea oil fields – Natural Radiation Environment Conference, NRE-VII, Rodos, 2002.

25. Chałupnik S., Wysocka M., - Oczyszczanie z radu wód KWK Ziemowit – dokumentacja zlecenia KWK Ziemowit, grudzień 2002, GIG Katowice.

26. Schonhofer F., - Liquid Scintillation Counting for environmental survey – International Conference on Advances in Liquid Scintillation Spectrometry, Karlsruhe 2001.

27. Wiegand J., - Radium behaviour in the environment – Hydrogeological Workshop NURAHYD-1, Luxembourg 2002.

28. Chałupnik S., - Badania wtórnego wymywania izotopów radu z osadów dennych – praca statutowa GIG, Katowice 2000.

29. Silva, N.C., Taddei, M.H.T., - Leaching assessment of radioactive and non-radioactive elements from Brazilian phosphogypsum - II International Symposium on Technologically

Enhanced Natural Radiation, September 1999, Rio de Janeiro, IAEA-TCDOC-1271, Vienna 2002.

30. Baza danych radiometrycznych Laboratorium Radiometrii GIG, wyniki badań stężeń izotopów radu w wodach, Katowice 2002 (niepublikowane).

31. Chałupnik S., - Leaching of radium from mine deposits with enhanced radium concentration – Int. Symposium NuRaHyd-1, Luxembourg 2002.

MEASUREMENT OF SHORT-LIVED RADON DAUGHTERS IN POLISH MINES

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INTRODUCTION

According to the Polish Regulations related to naturally occurring radiation hazards in underground mines, systematic monitoring of all recognised radiation sources has to be performed. Here, measurements of the potential alpha energy concentration (PAEC) of short-lived radon daughters are required (Skowronek et all, 1998). These obligatory measurements have been performed in the Polish underground mines since 1989. The most suitable methods are the so-called active methods when air is pumped through a filter that intercepts radioactive aerosols. Furthermore, the measurement of the activity of these collected “hot” particles makes it possible to evaluate the concentration of short-lived radon progeny in air. Depending on a chosen detection method one can measure the concentration of each short-lived radon daughter or only the PAEC.

In consideration of economical aspects, an attempt was made from the very beginning to combine it with measurements of the dust concentration. Therefore the developed measuring units were an integral part of the dust samplers complying with the requirements of the State Mining Authority to apply it in underground mines. This way the developed devices could fulfil two measurement tasks simultaneously: measurement of the dust concentration and potential alpha energy concentration of short-lived radon daughters. The new device based on the thermoluminescence detectors is able to cooperate with the dust samplers made by the Two-Met company and equipped with a cyclone making it possible to operate them constantly for one working day.

The location of this additional part inside the cyclone does not disturb the intrinsic safety of the whole construction and such a modified dust sampler can be used in the Polish underground mines and still preserve the common safety rules. Tests done with this unit showed that the lower limit of detection (LLD), using the membrane filters, was around 0.1 $\mu J \bullet m^{-3}$ at a 5% significance level, flow rate of 1.9 $dm^{3} \bullet min^{-1}$ and 1 hour pumping and 0.01$\mu J \bullet m^{-3}$ if pumping lasted 8 hours.

OPERATION DESCRIPTION

The Two-Met dust sampler configured to measure concentration of the respiration dust consists of a universal constant flow pump and the cyclone (Figure 1). The pump draws air through a filter with an adjusted flow rate ranging from 0.6 $dm^{3} \bullet min^{-1}$ to 2.2 $dm^{3} \bullet min^{-1}$. The device is supplied by a battery set and can operate continuously for at least 8 hours. The measurement run is supervised by a microprocessor. In the cyclone, the respirable dust is separated out and subsequently reaches a filter. The weight of this device is 550 g.

The flow rate of air going through the cyclone influences the class of dust that is separated out. This way a class can be chosen of particles reaching the filter that is contained in the cassette of the cyclone (Figure 1). According to criteria of the International Organisation for Standardisation (ISO) and the European Committee for Standardisation (CEN) concerning the sampling convention for aerosol, three fundamental classes of airborne dust can be specified (Figure 2). One of these is the already mentioned respirable class that includes particles able to reach the non-ciliary respiratory tract. The second, a so-called thoracic class is composed of particle penetrating beyond the larynx. The broadest class of particles that contains the two mentioned classes is the inhalable class. All airborne particles that can be inhaled through nose and mouth belong here. In case of the Tow-Met aspirator with the cyclone, at a flow rate of 1.9 $dm^3 \cdot min^{-1}$, particles with the median aerodynamic diameter (MAD) up to 8.5 μm reach the filter inside the cyclone what corresponds with the definition of the respirable dust. Very fine particle with diameter of the order of nanometers (unattached fraction and clusters) are intercepted by the cyclone inlet.

Figure 1. Aspirator AP-2000 EX

When the dust sampling is in progress, a resistance to air flow increases especially if the dust concentration is high. By excessive increase of the pressure drop the aspirator will be automatically switched off.

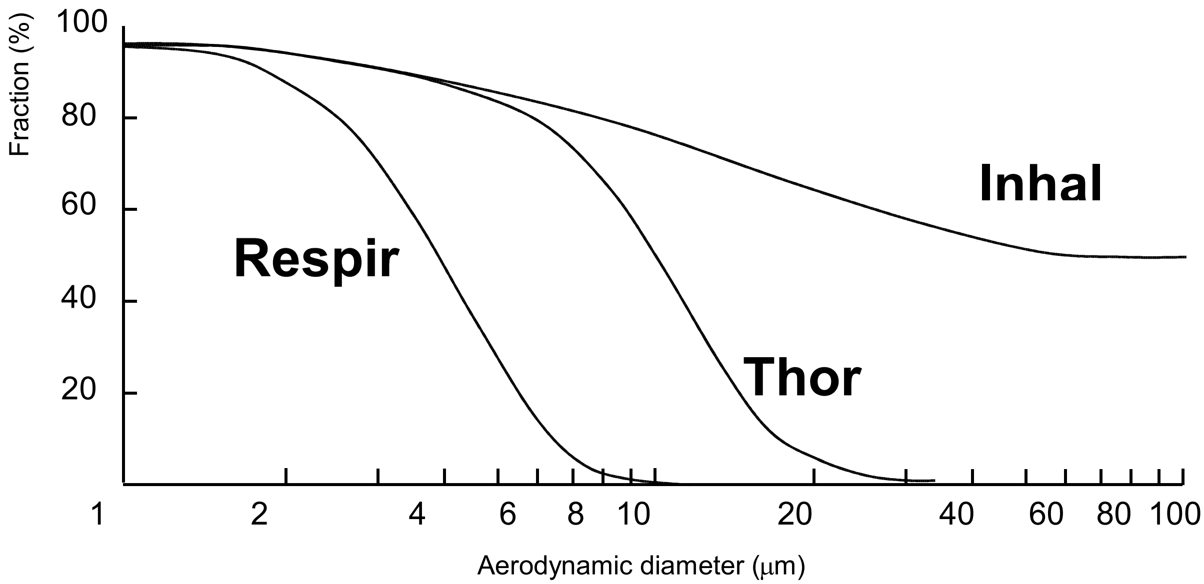

Figure 2. Fraction of the inhalable, thoracic and respirable particles in relation to all airborne particles according to ISO/CEN criteria.

The measuring device (Figure 3) is placed inside the cyclone cassette above the filter that intercepts the respirable dust. TL detectors are placed in three sockets and record radiation emitted by short-lived radon progeny bound up with the respirable dust. Each socket contains two DA-2 TL detectors. The first one, placed just above the filter, records the alpha- beta- and gamma radiation whereas the second one, separated with a spacer, can register only the beta- and gamma radiation. The outcomes received as a result of readouts of these TL detectors make it possible to evaluate the PAEC of short-lived radon progeny averaged over quite a long time. The location of the unit inside the cyclone does not disturb the measurement of the respirable dust concentration in air.

Polish Institute of Nuclear Physics in Cracow produces DA-2 TL detectors with diameter of 6mm and $CaSO_4$:Dy luminophore. The luminophore layer is 0.1mm thick. This layer is stuck on an aluminium base and so only one side of the TL detector remains active in relation to the alpha radiation. The luminophore has good efficiency, tens times higher than LiF:Mg,Ti, linear response up to 30 Gy and low fading, 1-2% within one month and 5-8% within one year (Niewiadomski, 1991). Readouts of these TL detectors were performed at a temperature of 265 °C and annealing at a temperature of 320 °C over 15 min. Temperature conditions during the annealing process do not have to fulfil such rigorous requirements as those of the TL detectors with LiF:Mg,Cu,P luminophore. The Da-2 TL detectors however have some shortcomings also. The most troublesome drawback is the progressive change of their sensitivity as a result of the luminophore crystals falling off from the aluminium base. However this effect becomes distinct after use of the TL detectors more than 10-15-times and then the device can be recallibrated.

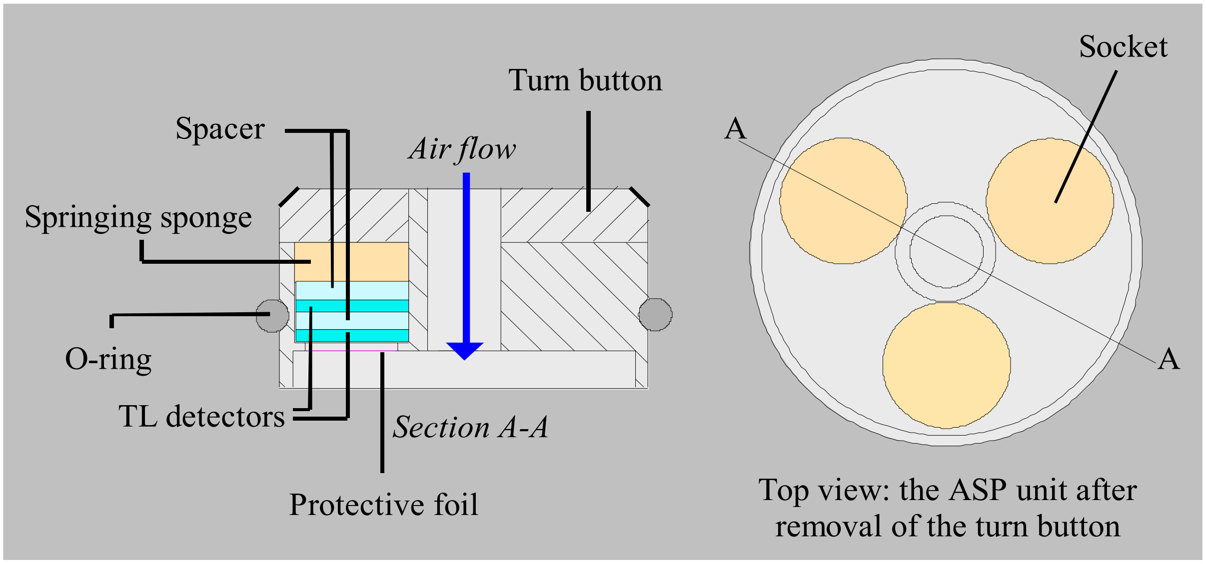

Figure 3. Sampling probe with the DA-2 TL detectors.

TESTING OF THE SAMPLING PROBE

Sensitivity of the measuring unit was proved in a radon chamber of 7.5 m^3. Water aerosols with activity median aerodynamic diameter of 3μm were injected into the chamber during the tests. The PAEC in the radon chamber was evaluated with the

help of the method described by Chalupnik et al (1985) . According to this method air is drawn through a filter. Afterwards the filter is immersed in a liquid scintillator to measure its activity according to the Thomas method (Thomas, 1970). On the basis of the results one can evaluate the PAEC in the radon chamber and calibration coefficient of the unit. The results are given in the next section.
Influence of the measuring unit on a measurement of the dust concentration was proved also. These tests were done in a dust chamber of 2 m^3.

During these tests a comparison between two sets of results was done. The first set of results was related to the dust concentration measurements performed by the aspirator equipped with the cyclone and measuring unit and the second related to the aspirator of the same type and configuration but without the additional measuring unit. The assessment of results was done on the base of EN Standard no 13205:2001. According to this, two dust samplers are admitted to have the same characteristics if the geometric standard deviation, calculated for two sets of results related to the compared aspirators, is below 1.3. The obtained value was around 1.03 so the differences can be regarded as statistically significant.

The cyclone inlet intercepts most of the very fine particles (unattached fraction and clusters) before they reach the filter. This was tested in the radon chamber of the Central Laboratory of Radioprotection (Warsaw, Poland) of 12.35 m^3. To fulfil this task impactors and diffusion battery screens were used. The obtained results show that this kind of inlet intercepts around 80% of particles characterised by the lognormal distribution with parameters: activity median diameter (AMD)=0.8 nm and geometric standard deviation σ_g=1.3.

The airflow is directed to a small area at the centre of the filter and the uniform dust distribution on the filter can be disturbed especially for the heavier particles (Figure 4). The geometry however enables the small area to be “observed” by the TL detectors too. The unit was additionally tested under field conditions. Such measurements were done in an underground mine both in the regions of dusty area near to long-walls being in progress and in the regions with relatively low dust concentration like water galleries and cross-cuts. No statistically significant differences were observed among results obtained from the developed measuring unit and any other devices where the impaction effect is not present.

Figure 4. The measuring unit Alfa-2000-Two Met and dust distribution on the filter.

LOWER LIMIT OF DETECTION AND MEASUREMENT UNCERTAINTY

In Table 1, values of the lower limit of detection are presented at a 5% significance level. In an ideal situation, readout of TL detectors could be done 3 hours after air pumping was finished, in the moment, when practically all short-lived radon daughters intercepted in the filter got disintegrated. However during the routine measurements when the devices are used in underground mines, the time period between preparation of TL detectors in a laboratory and readouts after performed measurements can reach 4 weeks. During this period, the signal related to gamma radiation increases and it means detection conditions are getting worse. Such cases are also taken into consideration too assuming the TL detectors were in a gamma radiation field of 0.07 $\mu Gy \bullet h^{-1}$ what is an average value in the Silesia district (Poland) outdoors.

The uncertainties were calculated assuming the PAEC: value is equal to 0.1 $\mu J \bullet m^{-3}$. For values higher than 0.5-1.0 $\mu J \bullet m^{-3}$ the increase of the pumping time does not improve measurement uncertainty essentially. Quite different situation can be observed for low values of the order of 0.1 $\mu J \bullet m^{-3}$. In this case, the increase of the pumping time from 1 hour to 8 hours will improve the measurement precision about 5 times.

In the described experiments, membrane filters (Pragopor-4) with pore size of 0.8 μm and fibre filters of type FIPRO-37 and FP/B3 were used. The sockets containing the TL detectors were protected with a polyethylene foil covered by the thin aluminium layer. The protective foil, placed from the side of the filter, has a surface density of 475 $\mu g \bullet cm^{-2}$.

Table 1. Lower limit of detection at a 5% significance level and measurement uncertainty at 95% confidence level. Measuring Device: Alfa-2000-Two-Met, flow rate 1.9 $dm^3 \bullet min^{-1}$, kerma rate free in air 0.07 μGy•.h-1.

Pumping time	Filter type					
	Pragopor 4		Fipro-37		FP/B-3	
	LLD	Uncertainty	LLD	Uncertainty	LLD	Uncertainty
	$[\mu J/m^3]$					
1 h	0.105	0.1±0.119	0.154	0.1±0.172	0.161	0.1±0.175
8 h	0.014	0.1±0.025	0.021	0.1±0.032	0.021	0.1±0.032
1 month	<0.004	0.1±0.014	<0.004	0.1±0.014	<0.004	0.1±0.014

The calculation of lower limit of detection (LLD) and measurement uncertainty in relation to was described more detaily by Skubacz and Bywalec (2003).

CONCLUSIONS

The combination of advantages of the TL detectors with measurement abilities of the Two-Met aspirators brought good results. The additional measuring device does not disturb the measurement of the dust concentration and enriches its measurement abilities. The measurement of the PAEC is not burdened with an important uncertainty that for value of 1 $\mu J.m^{-3}$ should not be worse than 10% for 1-hour pumping time and at a 95% confidence level. The lower limit of detection for 1-hour pumping time and routine measurements should not be worse than 0.2 $\mu J \bullet m^{-3}$ at a 5% significance level or 0.02 $\mu J \bullet m^{-3}$ for 8-hour pumping. Such sampling probe can be used for monitoring the naturally occurring radiation related to the short-lived radon daughters in the Polish underground mines.

REFERENCES

1. Skowronek, J., Skubacz K., Michalik, B., Kajdasz, R., Strzesniewicz, Z. *Monitoring and control of the radon hazard in Polish coalmines*. 1997. Proceedings of the 7th Tohwa University International Symposium - Radon and Thoron in The Human Environment - Katase, Fukuoko, Japan, 23-25 October 1997, Shimo [eds.]. World Scientific Publication, 446-454 (1998).
2. Niewiadomski, T. *Thermoluminescence Dosimetry in Practice*. Report no 1550/D. Institute of Nuclear Physics in Cracow. Cracow, Poland (1991).
3. Chalupnik, S., Skubacz, K., Lebecka, J. *A method of absolute measurement radon-daughter concentration in air*. Proceedings of the Third International Conference on Low Radioactiv*ity*, Bratislava 1985. Proceedings of Conference - Physics and Applications - Bratislava, 1985. VEDA, Publication House of the Slovak Academy of Sciences, Bratislava, Vol.13, 289-291 (1987).
4. Thomas, J.W. (1970), *Modification of the Tsivoglou method for radon daughters in air.* Health Physics, 19, 691 (1970).
5. Skubacz K., Bywalec T., 2003. Monitoring of the radiation hazard caused by short-lived radon daughters in mines. *Radiation Protection Dosimetry*. Vol. 103, No 3, p.241-246, Published by Nuclear Technology Publishing, Ashford, Kent, England, 2003

RADIUM REMOVAL FROM MINE WATERS 5 YEARS OF UNDERGROUND TREATMENT INSTALLATION

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Abstract

In underground coal mines in the Upper Silesian Coal Basin there are inflows of highly mineralised waters containing radium isotopes. These waters cause radioactive pollution of the natural environment in mining areas. Therefore cleaning of saline waters of radium is very important. Two types of radium-bearing waters were distinguished - one type containing radium and barium ions, but no sulphates (type A) and another one in which radium and sulphate ions are present but no barium (type B).

A very efficient and inexpensive method of purification of saline waters of Ba^{2+} and Ra^{2+} ions was developed and implemented in two coal mines. As the result of used technology, based on application of phosphogypsum as the cleaning agent, a

significant decrease of radium discharge was achieved - daily of about 120 MBq of ^{226}Ra and 80 MBq of ^{228}Ra.

Another type of radium waters does not contain barium ions, but contains sulphate ions SO_4^{2-}. There is no carrier for co-precipitation of radium so radium is transported with discharged waters to main rivers. Different method of purification from radium must be applied for such waters. Laboratory and field experiments were performed, and a cleaning method was chosen. For purification of saline waters - waste products from other industrial processes are applied. The method of purification has been applied in full technical scale in coal mine with very good results - approximately 6 m^3/min of radium-bearing waters are treated there. The purification takes place in underground old workings without any contact of mining crew with radioactive deposits, which are produced during the process. As a result amount of radium, released to the natural environment is significantly lower, more than 100 MBq of ^{226}Ra and ^{228}Ra remains underground each day. Purification has been started in May 1999, therefore a lot of experiences have been gathered during this period.

1. Introduction

In the coal mines of Upper Silesia, inflows of brines with enhanced natural radioactivity occur. In some cases, the total dissolved solids concentration (TDS) exceeds 200 kg/m^3, whilst the radium concentration may reach 400 kBq/m^3. The analysis of the radium isotopes in inflows showed, that the input of ^{226}Ra was of about 725 MBq per day, while the corresponding value for ^{228}Ra was roughly 700 MBq per day [Lebecka et al., 1986]. Only 40% of radium remained in the underground galleries and gauntons, whilst 60% were transported in pumped waters to the settling ponds on the surface and later to rivers [Lebecka et al., 1993, Lebecka et al., 1994]. It was an important source of contamination of the natural environment.

The phenomenon of the radioactivity of saline waters from coal mines in Poland was discovered in the1960’s [Sałdan, 1965]. Later, investigations showed, that radium concentration in water was correlated with the salinity [Tomza & Lebecka, 1981].

Moreover, two types of brine were distinguished in coal mines. In type A waters ions of barium and radium are present, while in type B waters only radium ions and sulphate occur, but no barium [Lebecka et al., 1986]. From type A waters radium is very easily precipitated out with barium carrier as sulphates after mixing with waters rich in sulphate ions. In type B waters there is no convenient carrier for radium, therefore no precipitation of radium scales occur. Further investigations showed, that discharge of radium-bearing waters from coal mines caused many cases of contamination of the natural environment, especially small brooks and rivers in the vicinity of these mines. The highest levels of contamination were always connected with release of type A waters and precipitation of insoluble deposits with enhanced radium content. Such process sometimes occurred in underground galleries but sometimes on the surface in settling ponds and small rivers, leading to the radioactive contamination of river beds. The purification of radium-bearing type A waters is based on the same chemical process. From waters of B type only a slow adsorption occurs, therefore the level of contamination is much smaller in comparison with type A waters.

In the past, the concentration as high as about 25 kBq/m^3 of ^{226}Ra in discharge waters from coal mines in Upper Silesia has been measured – and the total discharge approximately 900 MBq/day [Skubacz et al., 1990]. However, regulations demanded, that waters in which content of ^{226}Ra is more than 0.7 kBq/m^3 must be treated as a waste material with enhanced radioactivity [Decree of the Polish Atomic Energy Agency, 1989]. In Poland, at the beginning of 1990's in 10 out of 66 mines, such waters exceeded these limits. Type A waters were discharged from seven collieries, and type B waters from three. As a result of application of purification methods, at present two of the mines are allowed to discharge type A waters to the surface settling ponds. The total activity of ^{226}Ra in type A waters is only 30 MBq per day (reduced from 220 MBq/day). Three mines are sources of type B waters, but the amount of radium in such waters is much higher – about 180 MBq of ^{226}Ra per day [Wysocka et al., 1999]. Additionally, concentration of another radium isotope, ^{228}Ra, is even higher than that of ^{226}Ra, the total amount of this isotope in discharge waters is slightly more than 280 MBq per day.

The more stringent environmental regulations concerning radioactive discharges forced us to investigate the possibility of decontaminating the mine waters. The first task was to design the method for treatment of type A waters, which was relatively simple [Lebecka, Lukasik & Chalupnik, 1994]. Such method of radium removal have been implemented in two collieries in early 1990's, and have resulted in a substantial reduction in the amount of radium pumped to the surface – less than 55% of the previous value during period 1990 - 1995 [Michalik et al., 1999].

2. Occurrence of radium-bearing waters in coal mines in Poland

Investigations of techniques to purify radium-bearing type B waters were started in Laboratory of Radiometry of the Central Mining Institute in late 1980's. It was connected with important factors. On the basis of regulations, concerning permissible level of radium isotopes in waste water [The Decree of Polish Atomic Energy Agency, 1989], the local authority in Katowice issued a decision, that Piast Colliery was to make every effort to reduce as low as possible concentrations of natural radionuclides (radium isotopes) in waters, before discharging into Gostynka river. Moreover, the long-term release of radium-bearing waters that caused significant local contamination in settling ponds and small rivers, required the assessment of the ecological impact of radioactive pollution. Therefore this aspect of the possibility of radium removal from mine waters was also important.

Laboratory and field investigations on radium removal from mine waters were supported by Polish Committee of Scientific Research [Lebecka, Lukasik & Chalupnik, 1994]. Results, obtained during tests (also in underground galleries), and gave a firm basis for the design of the purification station in Piast Colliery [Chalupnik, 1999]. By 1996 the construction of the station had started, partly supported by National Fund of Environmental Protection and Water Resources. The construction of the installation was finished at the end of 1998 and testing started.

To aid the co-precipitation of radium, barium chloride was chosen as agent. During laboratory and field testing the capabilities of this agent have been proved. The chemical reaction is as follows:

$$BaCl_2 \Rightarrow Ba^{2+} + 2\,Cl^-$$

Firstly, the barium chloride dissolves in the water. Next step of the reaction is the co-precipitation of radium and barium ions as sulphates (in case of radium reaction is not stoichiometric):

$$Ba^{2+} + Ra^{2+} + 2SO_4^{2-} \Rightarrow BaRa(SO_2)_4$$

Unfortunately, there are some limitations on the use of that chemical. First of all, barium chloride is poisonous and the mining crew had to be trained in relevant safety procedures. Furthermore as well as other organisational and research activities, the background radiation level had to be checked prior to implementing the purification process both in underground galleries and on the surface.

In May 1999 an **Underground Purification Station (UPS)** in Piast Colliery started to work at the level -650 meters. This is unique, the only one underground installation for mine water treatment and removal of radium isotopes, built in non-uranium mine. Since July 1999 installation is used in a routine way to purify 6 m^3/min. i.e. 7 200 m^3/day of brines with enhanced concentrations of radium isotopes.

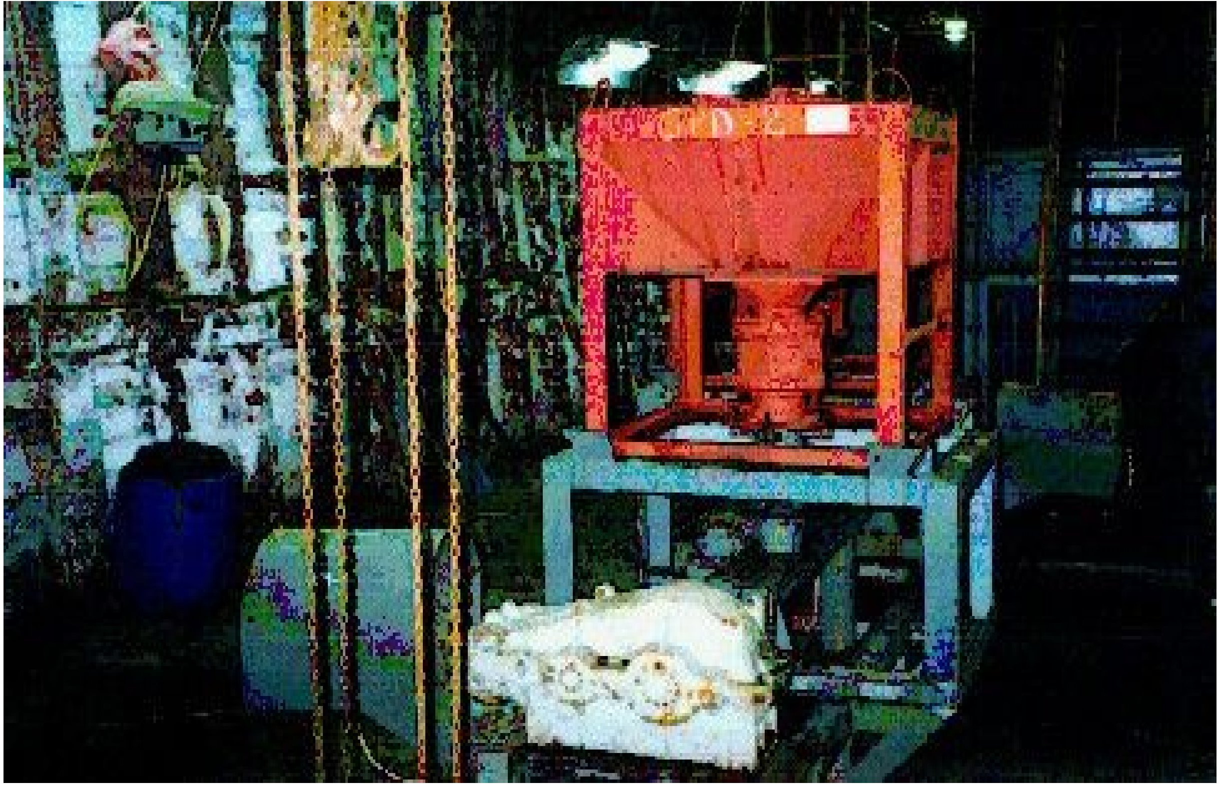
3. Underground treatment station – the construction

The whole system is located in the central part of the Piast Mine, in the vicinity of main shafts, at a depth 650 meters. This area was chosen by mine's geological service accordingly to the following reasons. First of all, although several development heading were driven in that area, the structure of coal seams was too complicated for the exploitation. Additionally, the coal quality from those seams was poor and numerous inflows of salty waters were found. Therefore the exploitation of coal in the area was stopped. Also very conveniently, that existing galleries in chosen area are beneath to the main galleries at the horizon, so no flooding would be caused by purification.

At first, the small gallery was prepared for the purification station. It had to be located close to the shafts and transportation galleries, to enable easy transport of cleaning agent. Water from the eastern part of the mine (3.5 m^3/min) is pumped to the purification station through 1500 metre long pipeline, but water from the western part flows along gutters and the flow rate is smaller – 2.6 m^3/min.

In the chamber of the purification station an automatic feeder of barium chloride was installed (see fig.1.). Water flows in the trough under the feeder, and the cleaning agent is fed into the water. In the gauton several baffles are built to make the water flow more turbulent. Under such conditions, the mixing of the barium chloride with water is better and the dissolution of barium chloride is faster as is the resulting co-precipitation of radium with barium carrier as sulphates. Water is removed from the chamber through a 600 metre pipeline (600 mm internal diameter) to the system of settling galleries. These are five parallel galleries each about 1050 m long and with a cross section of roughly 11.8 m^2. In these galleries the sedimentation of radium/barium deposits and of mechanical suspension takes place.

Fig.1 Underground treatment station - the feeder of the cleaning agent.



The settling galleries are isolated from the other parts of the mine. Special water dams were built, to ensure no leaking of the water to adjacent headings. Additionally, radioactive deposits in the system are confined and the radiation hazard for the miners is negligible.

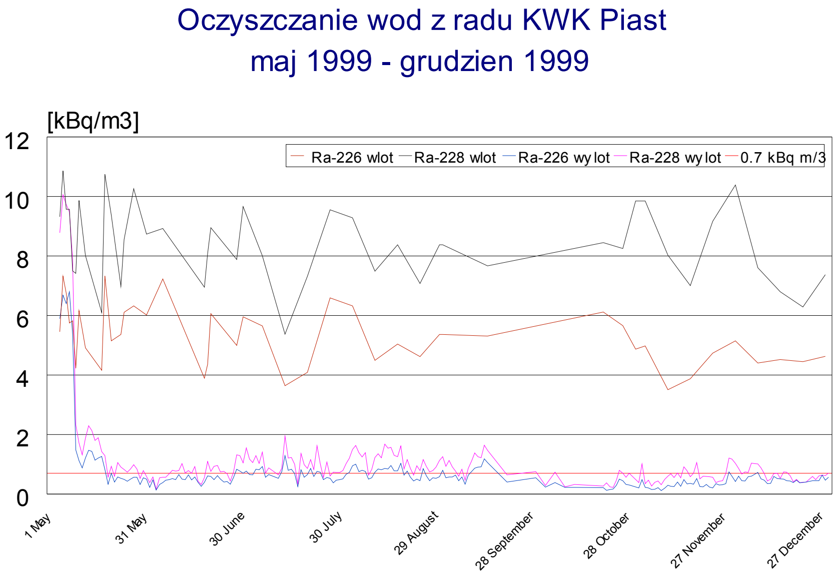
From the settling galleries water flows out to the main water galleries near the up-cast shaft and is pumped out to the surface, initially to Bojszowy reservoir and finally discharged to the Gostynka River.

4. Results of purification

The purification of mine waters was started in the Piast Colliery in May 1999. As the settling galleries were full of waters with enhanced radium concentration, so the feed of barium chloride during first ten days were carried out continuously, at the dose rate of about 100 grams per m^3. Since the volume in the settling galleries was assessed as 80000 m^3 and the daily inflow is approximately 10000 m^3 we did not expected to record any changes at the outflow until 6-8 days had passed.

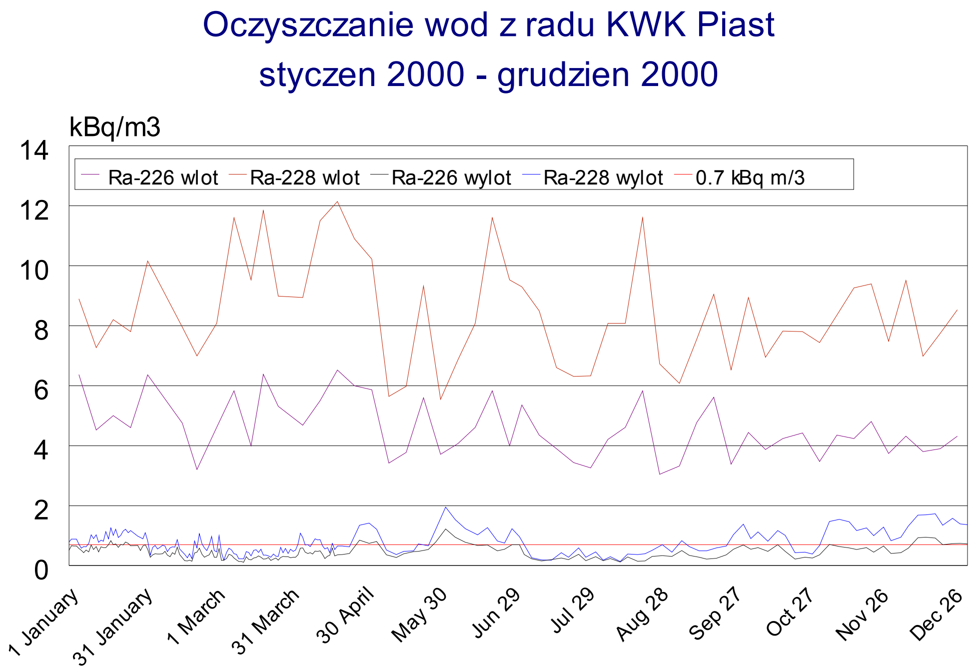
The radium content in water was monitored at several locations in the system. Water samples were taken from the inflow (before purification), and at the outflow from the system and from waters pumped to the surface. The Bojszowy reservoir was sampled every three months. Concentrations of radium isotopes in water (^{226}Ra and ^{228}Ra) were measured by means of liquid scintillation counting, preceded by chemical separation of radium [Chalupnik & Lebecka, 1993].

Fig.2. Results of purification in the year 1999



In fig.2. results of purification from the year 1999 are shown. Curves of ^{226}Ra and ^{228}Ra concentrations in the inflowing waters are plotted as well as similar curves for concentrations of radium isotopes in outflow from the system. One important thing must be pointed out – very good results of purification have been achieved quickly, within two weeks. The efficiency of treatment was 90% in average. It means, that the amount of radium isotopes in discharge waters decreased significantly - of about 40 MBq/day in case of ^{226}Ra and 65 MBq/day for ^{228}Ra. Total activity of radium isotopes, remaining daily in settling galleries of the system exceeded 100 MBq per day. In fig.3. results of purification in the year 2000 are shown. Very good efficiency of the purification can be easily seen.

Fig.3. Results of purification in the year 2000.



In table 1 results of monitoring for first two years are shown. In this period the average efficiency of treatment was at level 90%, slightly lower as predicted during laboratory and model experiments. The most important reason of such achievements was “human factor”, i.e. the influence of miners, maintaining the installation. The feeding of barium chloride must be continuous, any breaks affect the efficiency of the treatment. In circumstances of operating mine it is impossible to reach the same effects of purification as in the laboratory.

Table 1. Efficiency of underground purification of mine waters in Piast Colliery

Sampling site	^{226}Ra [kBq/m^3]				^{228}Ra [kBq/m^3]			
	Min.	Max.	Average	Median	Min.	Max.	Average	Median
Inflow into UPS	3.51	7.33	5.20± 0.93	5.02	5.77	10.75	8.27± 1.21	8.22
Outflow from UPS	0.05	1.47	0.55± 0.24	0.53	0.05	2.29	0.86± 0.37	0.80
Efficiency of purification [%]			≈90				≈90	

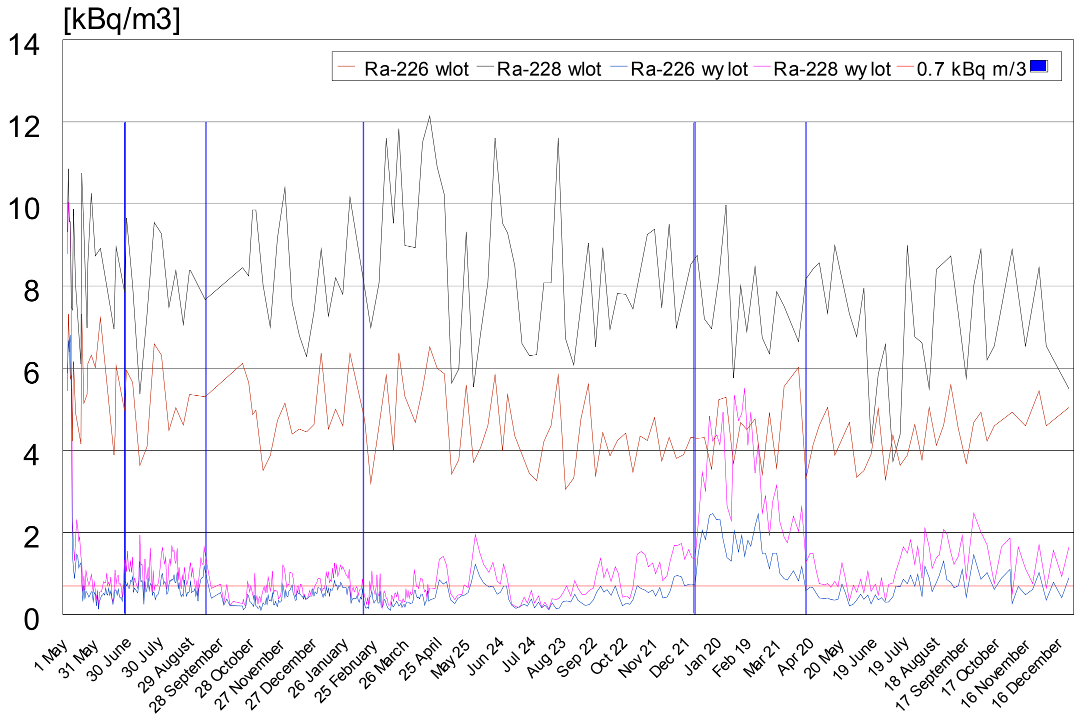


Fig.4. Results of water treatment in the Piast Colliery in the period May 1999 - December 2001.

In fig. 4. results of water purification in the period 1999 -2001 are shown. Vertical bar are markers of important events during treatment of brines at UPS. At the end of June 1999 the start-up of the installation was finished formally, and probably due to less careful maintenance and supervising of experts became not so intense as previously. The immediate increase of radium content at the outflow was observed. After additional training of the staff, efficiency of purification increased. But again, at the end of the 1999, we observed worsening of the results. Therefore the increase of the amount of barium chloride, fed daily into water (from 500 kg to 750 kg) was ordered with positive results. In the year 2001 the amount of used cleaning agent was 250 kg per day only within first 3 months and 500 kg later on. The only reason was financial – problems with payment for the barium chloride caused the decrease of the efficiency of purification. Since the beginning of 2002 financial problems were solved.

5. Influence of the purification on the environmental pollution

We started to measure radium concentration in waters, discharged from the Piast Mine into the Gostynka River, several years ago [Lebecka et al., 1986] and the contamination in the vicinity of Bojszowy reservoir and of the river's bed has been investigated more recently [Wysocka et al., 1999]. During this period we gathered a lot of data, on which we can assess the effects of purification. In fig.3. results of measurements of radium concentration in waters from different sampling points are shown. We measured radium content in waters from main water galleries at 650 meters level, in discharge waters from the Piast Mine at its settling pond on the surface, as well as in waters released from settling pond into the Gostynka River, and the results are shown in Figure 5.

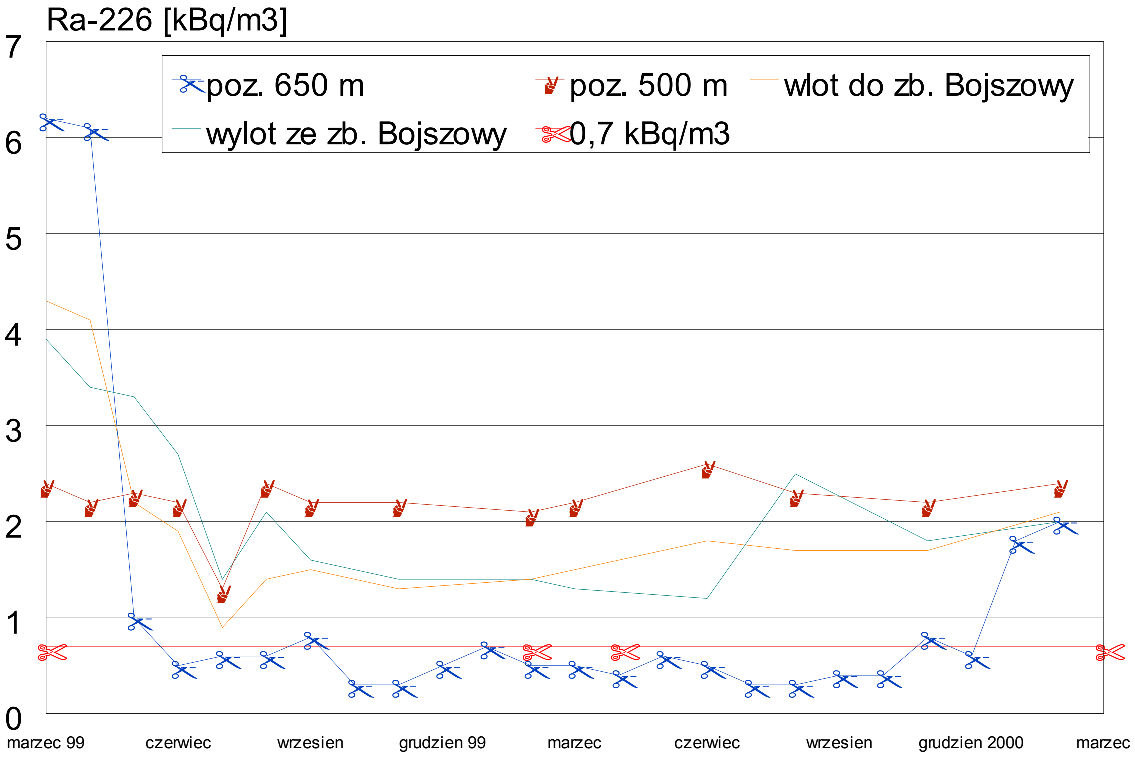


Fig.5. Results of the purification on the surface in the period 1999 – 2000.

During the start-up of the purification, the effect of radium removal was significant. In cumulative waters from the 650 meters level the concentration of radium isotopes $^{226}Ra+^{228}Ra$ decreased from 15 kBq/m^3 down to the value 1.5 kBq/m^3. It means, that the amount of radium, pumped onto the surface from that horizon is reduced by a factor of ten (see fig.5.).

Such a major decrease of radium concentration in waters from 650 meters level resulted in a decrease in the waters from settling pond on the surface. However the results are not commensurate, because 500 meters level waters are not treated yet. The assessment of the radium balance showed, that the amount of radium released into the pond was about 65% lower compared with previous values. As expected, the same pattern was observed at the outflow from the pond, but slightly retarded due to the retention time in the pond of roughly 8-9 days.

Nonetheless, the radioactive contamination of waters, discharged into the Vistula River was significantly diminished as a result of the implementation of the purification method. Calculations, made on the basis of actual measurements, leads to the conclusion, that the total amount of ^{226}Ra, released through Gostynka to the Vistula river is 45 MBq/day lower than before, whilst corresponding value for ^{228}Ra is 60 MBq/day. The decrease in discharge of both radium isotopes from the Piast Colliery into the natural environment by saline waters is above 100 MBq per day.

6. Possibility of barium chloride application in liquid form

The idea of application of barium chloride in a liquid form appeared as a solution of two main problems of brines treatment. Firstly, feeders of solid barium chloride were built as heavy-duty prototypes and after several years it is more and more difficult to repair mechanical damages. Secondly, results of purification with use of solid cleaning agent are vulnerable to not proper maintenance. Moreover, in several mines feeders of liquids are used for coagulants and flocculants to remove mechanical suspension from mine waters. Such units are commercially available and permitted to be installed in underground galleries. Application of the feeders of the solution of cleaning agent will enable an automatic treatment of brines and decrease of the hazard of casual inhalation of toxic barium chloride. Transportation of the solution from the surface to the installation should also be safer.

First stage of the investigations was laboratory tests of efficiency of the barium chloride solution. For the investigations mine waters from different mines, with different mineralization and radium content have been used. Several series of purification have been performed, with different contact time, loads of the cleaning solution etc. Results are shown in fig. 6.

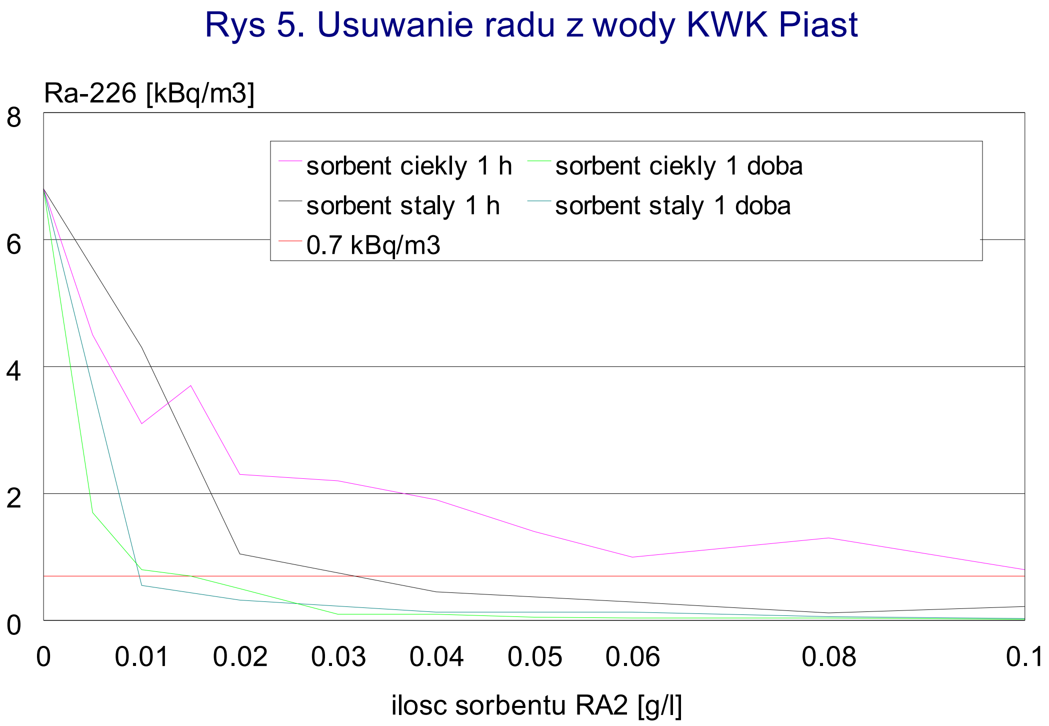


Fig.6. Radium removal from mine water with application of barium chloride solution – results of laboratory tests.

It can be seen that efficiency of barium chloride in solid and liquid form is similar, especially for the longer time of the contact. Differences for a short time of contact were mainly due to the problem of the filtration of fine crystals of barium sulphate from the brine after treatment. For the contact time 24 hours no differences were observed bigger than uncertainties of the results. Therefore a conclusion can be drawn, that efficiency of liquid form of barium chloride is the same as efficiency of solid barium chloride. Field experiments are necessary to confirm results of laboratory investigations.

SUMMARY

The purification station in Piast Colliery is unique, it being first underground installation for the removal of radium isotopes from saline waters. Therefore there was no previous experience to fall back on concerning construction, application and management.

The implementation of this method of purification of radium bearing waters in non-uranium mine was difficult. All elements of the system – sedimentation galleries, feeders, control units etc. had to be designed without any comparison with other similar systems. In particular the proper organisation of the transport of poisonous substance from the surface to the chamber within an operating coal mine was very important. On the other hand, observations and experience gathered during the implementation of the method will be advantageous in the future, and will aid in the planning and development of similar systems in other coal mines.

The ecological effect of the purification is also important. On the surface, at the inflow of saline waters into the settling pond, as well as at the outflow from that pond, concentrations of radium isotopes are approximately 60-65% lowers than before purification. It corresponds to the decrease of about 45 MBq for ^{226}Ra and 60 MBq for isotope ^{228}Ra of daily release from the Piast Mine. It means, that the total amount of radium, discharged into the Gostynka and Vistula rivers is much lower, by a value 105 MBq/day.

To achieve the complete radium reduction in mine waters from the Piast Colliery, the removal of radium isotopes from waters at 500 meters level must be undertaken. We plan to use the existing installation for this purpose in the near future, firstly for waters with the highest concentrations of radium, later on for all radium-bearing waters from that horizon.

The implementation of the method and technology of mine waters purification was awarded in the year 2000 by Ministry of the Environment for the outstanding scientific achievement in the field of environmental protection. In 2001 Central Mining Institute obtained a certificate of President of Poland for the Best Available Technology.

A new concept of the feeding of the barium chloride as been developed to override problems with “human factor” influence on the purification results. This idea seems to be a solution to design fully automatic feeder and implement treatment technique in other collieries in Upper Silesia region. First implementation will be another horizon in Piast Mine (-500 meters).

Till now laboratory experiments have been performed with very promising results, confirming possibility of application of liquid cleaning agent with similar efficiency as solid barium chloride.

References

1. Zarządzenie Prezesa PAA z dnia 19 maja 1989 w sprawie zasad zaliczania odpadów do odpadów promieniotwórczych - Monitor Polski nr 18 poz. 125, Warszawa 1989.

2. Lebecka J. i wsp. - Metoda i technologia oczyszczania z radu wód typu B - dokumentacja grantu celowego KBN, Katowice 1994.
3. Dokumentacja nr 35081 pt. Projekt techniczny. System oczyszczania wód dołowych za radu na poz. 650. Części: mechaniczna, górnicza, elektryczna. Biuro Studiów i Projektów Górniczych w Krakowie, 1995.
4. Chałupnik S., Wysocka M., Wstępne wyniki oczyszczania wód dołowych z radu w KWK Piast, efekty I etapu wdrożenia, Dokumentacja GIG, Katowice, 1999.
5. Lebecka J., Chalupnik S., Lukasik B., Wysocka M., - Monitoring and Control of Radioactive Contamination of Natural Environment Caused by Mining Activity, Proc. of Int. Conference Ecological Aspects of Underground Mining, Szczyrk, Published by Central Mining Institute, Katowice, Poland, p. 198, (1993).
6. Tomza I., Lebecka J., - Radium-bearing waters in coal mines: occurrence, methods of measurements and radiation hazard - Int. Conf. On Radiation Hazards in Mining, Golden, Co, 1981.
7. Lebecka J. i wsp. - Skażenia promieniotwórcze na Górnym Śląsku powodowane przez wody kopalniane i wytrącające się z nich osady -Wiadomości Górnicze, 6/91, Katowice 1991.
8. Lebecka J. I wsp., Radioactivity of Mine Waters in Upper Silesian Coal Basin, and its Influence on Natural Environment, Mine Water Congress, Nottingham, 1994.
9. Chałupnik S., Wysocka M., Wyniki badań nad oczyszczaniem wód dołowych KWK Czeczott z radu – Dokumentacja GIG, Katowice 1996.
10. Urząd Patentowy RP – Patent nr 169869 na :Sposób oczyszczania wód z radu", dla zespołu pod kierownictwem dr J. Lebeckiej.

RADIUM BALANCE IN DISCHARGE WATERS FROM COAL MINES IN UPPER SILESIA REGION

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Abstract

Saline waters from underground coal mines in Poland often contain natural radioactive isotopes, mainly ^{226}Ra from the uranium decay series and ^{228}Ra from the thorium series. Approximately 60% of the total amount of radium remains underground as radioactive deposits, but 120 MBq of ^{226}Ra and 200 MBq of ^{228}Ra are released daily into the rivers along with the other mine effluents from all Polish coal mines. Technical measures such as inducing the precipitation of radium in gobs, decreasing the amount of meteoric inflow water into underground workings etc., have been undertaken in several coal mines, and as a result of these measures the total

amount of radium released to the surface waters has diminished by about 60% during the last 5-6 years.

Mine water can have a severe impact on the natural environment, mainly due to its salinity. However associated high levels of radium concentration in river waters, bottom sediments and vegetation have also been observed. Sometimes radium concentrations in rivers exceeded 0.7 kBq/m^3, which was the permitted level for waste waters under Polish law. The extensive investigations described here were carried out for all coal mines and on this basis the total radium balance in effluents has been calculated. Measurements in the vicinity of mine settling ponds and in rivers have given us an opportunity to study radium behaviour in river waters and to assess the degree of contamination.

Introduction

Very often human activity, connected with the exploitation of mineral resources, leads to the contamination of the natural environment. Sometimes natural radionuclides are released or concentrated as waste material. In Poland the main source of waste and by-products with enhanced concentration of natural radionuclides is power industry, based on the coal exploitation and combustion. In hard coal mining industry 50 million tons of different waste materials are produced annually. As a result of coal combustion in power plants, the area of fly ash and sludge piles is increased by several km^2 per year [Michalik et al., 1995].

Upper Silesian Coal Basin (USCB) is located in the Southern-West part of Poland. Presently there are 66 underground coal mines there extracting approximately 150x10^6 tons of coal per year. The depth of mine workings is from 350 to 1050 m. Upper Silesia is characterized by a very complicated and differentiated geological structure with numerous faults and other tectonic dislocations [8]. Additionally, the area is very affected by mining

Two hydrological regions of the Coal Basin have been distinguished. First region is located in southern and western Silesia with thick strata of sediments covering carboniferous formation. This overlay is built mainly by Miocene clays and silts. The thickness of this rocks is up to 700 m. Such strata make almost impossible migration of water an gases. In the second region Miocene clays do not occur. Carboniferous strata are covered by and Quaternary sediments, slightly compacted.

The oldest formations of this area form isolated sediments of Permian or Triassic limestone strongly fissured. There are numerous outcrops of coal seams. These formations enable very easy migration of water and gases.

An additional and unexpected component of the radioactive contamination of the natural environment, and different from that usually associated with this kind of industry, is caused by underground coal exploitation. In many of coal mines, located in Upper Silesian Coal Basin waters with enhanced radium content occur [Lebecka et al., 1986]. Sometimes in radium-bearing brines barium ions are also present, in concentrations up to 2 g/l. Such waters were classified as radium-bearing type A waters. On the other hand, in the second kind of waters, which have been called type B, no barium can be found but radium and sulphate ions are present.

In the area of Upper Silesian Coal Basin (USCB) operate of about 40 underground coal mines. The total water outflow from these mines is about 800 000 m^3/day. The salinity of these brines is far higher than that of ocean water. The total amount of salt (total dissolved solids - TDS) carried with mine waters to the rivers is about 10 000 tonnes/day. The commonest ions in these brines are Cl^- and Na^+ with concentrations up to 70 g/l and 40 g/l respectively, additionally brines usually contain several grams per litre of Ca^{2+} and Mg^{2+} and significant amounts of other ions [Tomza & Lebecka, 1981]. Waters with high radium concentration occur mainly in the southern and central part of the coal basin, where coal seams are overlaid by a thick layer of impermeable clays [Rozkowski & Wilk, 1992]. These saline waters cause severe damage to the natural environment, owing mainly to their high salinity (sometimes > 200 g/l), but also their high radium concentration, reaching 390 kBq/m^3 [Skubacz et al., 1990].

The presence of barium in waters is the most important factor for the further behaviour of radium isotopes in mine galleries or on the surface. From type A waters radium and barium always co-precipitate as sulphates, when such waters are mixed with any water containing sulphate ions. As a result of the precipitation, barium sulphate deposits with highly enhanced radium concentrations are formed [Lebecka et al., 1986, Michalik et al., 1999]. The total activity of radium isotopes in these sediments may sometimes reach 400 kBq/kg. In comparison, average radium content in soil is 25 Bq/kg [UNSCEAR, 1982]. In case of radium-bearing type B waters, no precipitation occurs due to the lack of the barium carrier, and that is why the increase of radium content in sediments is much lower that ones originated from type A waters.

Applied methods and instrumentation.

Radioactivity of waters from coal mines is mostly from radium isotopes - ^{226}Ra from the uranium series and ^{228}Ra from the thorium. A method of chemical separation of radium, developed by Goldin [Goldin, 1961], has been modified for liquid scintillation counting [Chalupnik & Lebecka, 1990; Chalupnik & Lebecka, 1993]. Radium is co-precipitated with barium in form of sulphates and this precipitate is mixed with liquid gelling scintillator. The prepared samples were measured by a low background liquid scintillation spectrometer (QUANTULUS, Wallac Oy, Finland). This counter is equipped in alpha/beta separation and anti-coincidence shield, which enables measurements of ^{226}Ra concentration above 3 Bq/m^3 with simultaneous measurements of ^{228}Ra (LLD = 30 Bq/m^3) and ^{224}Ra (LLD = 50 Bq/m^3). In addition, the procedure enables the simultaneous preparation of ^{210}Pb, which can separated from radium isotopes at the last stage of analysis and also measured in the LS spectrometer with a detection limit of 20 Bq/m^3.

3. System of monitoring in the vicinity of coal mines

In the mining industry in Poland, monitoring of the radioactivity of mine waters, precipitates as well as gamma doses is obligatory since 1989.

Monitoring of radioactive contamination caused by effluents and tailings from coal mines must be done since 1986 [9]. Due to these regulations the following measurements must be done in mine's vicinity:

I. The concentration of ^{226}Ra and ^{228}Ra in effluent from the settlement pond, in river above and below the discharge point, in water supplies nearby discharge point.

II. The concentrations of natural radionuclides in solid samples, dumped onto the piles.

Such complex monitoring system gives an opportunity to obtain a complete picture of the influence of a certain mine on the underground and surface employees as well as on inhabitants of adjoining areas.

Concentration of radium isotopes in original water samples from different coal mines varies in a very wide range - from 0 to 110 kBq/m^3 for ^{226}Ra and from 0 to 70 kBq/m^3 for ^{228}Ra [10]. In 80's waters with radium concentration above 1.0 kBq/m^3 were found in 43 out of 65 coal mines in Upper Silesian Coal Basin. The highest concentrations of radium were measured in highly mineralised waters from deeper levels in radium-bearing waters type A. The ratio of ^{226}Ra to ^{228}Ra in radium-bearing waters type A was in average of about 2:1. Contrary in radium-bearing waters type B there were more ^{228}Ra than ^{226}Ra, the ratio ^{226}Ra: ^{228}Ra was from 1:2 up to 1:3. Concentration of ^{226}Ra in these waters reached 20 kBq/m^3, while maximum concentration of ^{228}Ra was as high as 32 kBq/m^3. These values justify the statement that Upper Silesian radium-bearing waters belong to the waters with highest known radium concentration.

Requirements of the mine waters monitoring are shown in table 1.

Table 1. Frequency of monitoring of discharge waters in Poland

Sampling site	Monitoring requirements	Frequency of monitoring
Discharge waters from underground workings at the inflows and outflows of surface settling ponds	All mines	Once a year
	If concentration of ^{226}Ra + ^{228}Ra in discharge waters exceeds 0.7 kBq/m^3	At least once per quarter
Discharge points into rivers	All mines	Once a year
	If concentration of ^{226}Ra + ^{228}Ra in discharge waters exceeds 0.7 kBq/m^3	At least once per quarter
River water upstream and downstream from discharge points	All mines	Once a year
	If concentration of ^{226}Ra + ^{228}Ra in discharge waters exceeds 0.7 kBq/m^3	At least once per quarter
Underground waters for drinking or utilization	All mines	Once per 6 months
Surface wells possibly influenced by discharge of brines	If concentration of ^{226}Ra + ^{228}Ra in discharge waters exceeds 0.7 kBq/m^3	At least once per quarter

Original waters flowing into mine workings from the rocks from different aquifers are collected in gutters in underground galleries, brought together from different parts of the mine, clarified and pumped out to the surface. Radium concentration in these mixed waters was lower than in original water and did not exceed 25 kBq/m^3 of ^{226}Ra and 14 kBq/m^3 of ^{228}Ra [10].

Basing on the results of measurements of radium concentration in the original waters inflows into the mine workings and on data on the flow rates of water provided by the mine hydrologists, the total activities of both radioisotopes of radium flowing with water to different parts of mines and to different mines were calculated. This results were compared with values obtained using radium concentrations in mixed waters taken from the drainage system (from gutters) from different parts of mines and corresponding flow rates obtained from the mines. The difference is indicating the activity of radium remaining in underground mine workings due to spontaneous precipitation of radium and barium sulphates or due to applied purification of water. The calculated activity of radium remaining in underground mine workings as deposits in all Upper Silesian coal mines is 525 MBq/day of ^{226}Ra and 480 MBq/day of ^{228}Ra. These values can not be considered as very accurate, since the uncertainty of measurements of flow rates of small inflows is rather large. The approximate amount of ^{226}Ra in **water inflows in coal mines** in USCB have been calculated as high as 650 MBq/day (i.e. 230 GBq per year) while for ^{228}Ra this value is of about 700 MBq/day or 255 GBq per year. Although radium concentrations in waters type B are usually lower than in waters type A the total inflows to mines where radium-bearing waters type B occur are much higher. As a result the total activity of radium carried with water type B is higher. The highest values for a single mine (with waters type B) are: 78 MBq per day of ^{226}Ra and 145 MBq per day of ^{228}Ra.

In comparison corresponding values of inflows of radium with saline waters in 4 copper mines in Poland are: 31 MBq of ^{226}Ra and 3 MBq of ^{228}Ra per day.

4. Assessment of radium balance in discharge waters

One of the biggest advantages of the monitoring system in Upper Silesia region is a possibility to make an assessment of radium balance in discharge waters periodically. For instance in years 2002 and 2003 such assessments have been prepared. For the calculations of about 300 results of mine waters have been taken as well as 40 analyses of river waters. The term „mine waters" means not only mine waters but also river waters close to the discharge points. Term “river waters” is used for the samples taken at the sampling points of regional monitoring system of water quality. All the data are included in the mine waters database in the Laboratory of Radiometry as the element of the radiation hazard monitoring and environmental monitoring. A comparison of assessment results in chosen periods is shown in table 1.

The assessment of the total activity of radium released from coal mines in Upper Silesia with waste water is based on:

- results of determination of radium isotopes in waters released by collieries;
- data on amount of water released by individual mines.

We have also made an estimation of total activity of radium which remains in underground workings in a form of deposit precipitated out of radium-bearing waters either due to unintended mixing of natural waters of different chemical composition or due to the purification of radium-bearing waters. This estimation has been done basing on:

- results of determination of radium isotopes in original waters inflowing to the underground mine workings from the rocks;
- rough estimation of the amounts of water inflows from different sources or parts of mines;
- calculated value of the total activity of radium pumped out from underground mine workings with waste waters by individual mines.

Much more accurate are the results of calculations of the total activities of radium present in water pumped out from individual mines. These values were calculated basing on the radium concentration determined in these waters and on data of amount of water provided by mines.

Samples of discharged waters were taken from settling ponds. In outflows from thses ponds in 87 % mines ^{226}Ra concentration exceeds 0.008 kBq/m^3, in 25% ^{226}Ra concentration is higher than 0.1 kBq/m^3 and in 8 % exceeds permissible level - i.e. 0.7 kBq/m^3 [9].

In rivers enhanced concentrations of radium can be observed many kilometres down from the discharge points. This is mainly true for radium-bearing waters type B, because out of these waters radium is not easily precipitated. The highest value of ^{226}Ra concentration was as high as 1.3 kBq/m^3 - it was found in a small stream near it's conjunction with Vistula river.

Table 2. Comparison of radium balance assessment in rivers from Upper Silesia region

Catchment area	Total activity **1987** [MBq/day]	Total activity **1995** [MBq/day]		Total activity **2003** [MBq/day]	
	^{226}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Inflows into "OLZA" pipeline from 11 mines	**261.8**	**9.8**	**6.7**	**6.8**	**6.8**
Olza River – discharge of „Olza" pipeline	**35.4**	**1.6**	**1.4**	**2.5**	**1.8**
Ruda-Nacyna Rivers (3 mines)	**4.8**	**2.2**	**1.4**	**0.7**	**0.7**
Bierawka River (5 mines)	**7.4**	**1.6**	**1.2**	**2.7**	**3.2**
Bytomka River (5 mines)	**0.6**	**0.4**	**0.5**	**1.5**	**3.0**
Kłodnica River (7 mines)	**7.3**	**2.6**	**2.9**	**2.6**	**3.7**
Rawa River (4 mines)	**0.7**	**0.2**	**0.2**	**1.2**	**2.7**
Brynica River (4 mines)	**1.1**	**0.0**	**0.0**	**1.4**	**2.4**
Przemsza River (2 mines)	**7.8**	**0.4**	**0.8**	**2.3**	**5.6**
Bobrek River (3 mines)	**4.0**	**0.2**	**0.2**	**0.3**	**1.2**

Catchment area	Total activity **1987** [MBq/day]	Total activity **1995** [MBq/day]		Total activity **2003** [MBq/day]	
Black Przemsza River (4 mines)	**1.2**	**1.6**	**3.1**	**1.3**	**2.3**
Gostynka River (3 mines)	**224.6**	**133.9**	**248.1**	**61.1**	**146.7**
Mleczna River (2 mines)	**0.7**	**1.3**	**2.4**	**1.5**	**3.3**
Upper Vistula (4 mines)	**191.8**	**73.0**	**117.2**	**42.9**	**84.2**
Total: 35 active mines 30 abandoned	**397.7**	**219.1**	**380.1**	**120.1**	**258.2**

The significant decrease of daily discharge of radium can be seen in the period 1987 -1995. There were two reason of this effect. Firstly, the purification of A type mine waters has been started in several coal mines in catchment areas of Olza river and Upper Vistula. The another reason was due to economical changes in the mining industry – dewatering of deep mines was more and more expensive and hydro-technical solutions have been applied in numerous mines to reduce water inflows into underground galleries, with special emphasis on brines.

In the last period the decrease of radium activity in discharge waters is mainly due to the purification of B type brines in Piast Colliery. The implementation of the treatment technology on deeper of the horizons in the mine caused the decrease of radium release from the mine at level 150 MBq/day – 60 MBq/day of ^{226}Ra and 90 MBq/day of ^{228}Ra. The application of the purification technology in another mine should further reduce radium discharge. Construction of the system has been already started. Additionally, purification system for second horizon of Piast mine is under designing, and it will solve most of the problems with radium contamination of river waters in Upper Silesia region.

Enhanced radium concentrations are mainly observed in the Vistula river, into which most of the radium is discharged with B type waters - approximately 110 MBq of ^{226}Ra and 250 MBq of ^{228}Ra per day. Concentration of ^{226}Ra (0.035 kBq/m^3) was observed in Vistula in Cracow - 70 km downstream from Upper Silesia. Some of these waters are not discharged directly to Vistula river, but to it's tributaries. The influences of singular inflows can be seen very clearly. Moreover, waters from first mine are A type and the difference of radium behaviour (fast precipitation) in comparison with other 3 mines (waters B type) is very evident. Different situation was observed in the vicinity of Oder river, where in coal mines occur mainly waters type A. The amount of radium discharged into this river is much lower - 10 MBq per day of ^{226}Ra and 5 MBg/day of ^{228}Ra. As a result concentrations of radium in Oder ***are below 0.1 kBq/m^3.***

Concentrations of radium isotopes in some rivers in Upper Silesia are clearly enhanced as compared with natural levels. In comparison with data from other locations, concentrations of radium isotopes in rivers in USCB are significantly higher. Enhanced concentrations of radium in river waters in Upper Silesia are caused solely by the influence of mine waters.

Due to release of radium-bearing mine waters from coal mines there is a contamination of river waters. As a result radium concentration in some small rivers exceeds permissible level for radioactive wastes. Therefore development and application of purification methods is justified and further efforts should be done to reduce the contamination of rivers, particularly of Vistula River and it's tributaries.

On the other hand we must take into account, the exploitation of deeper coal seams will cause more problems with inflows of radium-bearing brines into underground workings, even in these mines where no radium problems exist right now. Therefore periodical monitoring of discharge waters is necessary. Another legal problem must be also solved - responsibility for monitoring of waters, released from abandoned mines

8. Summary

- Coal mining may cause significant pollution of the natural environment due to release of waste waters with enhanced concentrations of natural radionuclides (mainly radium isotopes. This phenomenon is well known not only in Upper Silesian Coal Basin but also in other regions of underground exploitation of coal (Ruhr Basin), oil and gas or other resources.
- Due to mitigation measures, undertaken by mines, the significant improvement can be observed during last two decades. In most cases radium concentrations in discharge waters are low and surface waters are not contaminated. Moreover, further decrease of radium release is predicted as a result of underground mine water purification in two collieries.
- Monitoring system of natural radionuclides in waste waters and river waters is an important element of the prevention against the pollution of the natural environment. Moreover, it is a source of data for optimization of ground reclamation of previously contaminated areas (mainly settling ponds) of abandoned coal mines.

Of course, further improvement of the system is required as well as solution of important legal problems, related with liquidation of coal mines, harmonization with EU regulations etc.

References

WYSOCKA M. i inni: *Bilans ładunków substancji promieniotwórczych w dopływach wody do kopalń węgla kamiennego i kopalń zagłębia miedziowego.* Dokumentacja GIG w ramach projektu celowego KBN *STRATEGIA I DZIAŁANIA OGRANICZAJĄCE ZASOLENIE WÓD, Główny Instytut Górnictwa,* Katowice 1995.

Skowronek J. i inni: *Źródła narażenia radiacyjnego w kopalniach węgla*. W: Monografia „Naturalna promieniotwórczość w środowisku", rozdział 3, Główny Instytut Górnictwa, Katowice 2003 (w druku).

Zgadzaj J., Skubacz K., Chałupnik S.: *The influence of radon and it's progeny emitted from the exhaust shafts of coal mines on the contamination of the outdoor air.* International Conference "Technologically enhanced natural radiation caused by non-uranium mining", Katowice, Główny Instytut Górnictwa 1996.

Lebecka J., i inni: *Monitoring of Radiation Exposure from Different Natural Sources in Polish Coal Mines.* International Conference on Occupational Safety in Mining, Vol.2, Toronto, Canadian Nuclear Association 1985.

Skubacz K., Lebecka J., Chałupnik S., Wysocka M.: *Possible changes in radiation background of the natural environment caused by coal mines activity.* International Symposium on Nuclear Techniques in Exploration and Exploitation of Energy and Mineral Resources, IAEA-SM-308, Vienna, IAEA 1990.

KOSTER H.W., MARWITZ P.A., BERGER G.W., VAN WEERS A.W., HAGEL P.: *^{210}Po, ^{210}Pb, ^{226}Ra in Aquatic Ecosystems and Polders, Anthropogenic Sources, Distribution and Enhanced Radiation Doses in the Netherlands.* The Natural Radiation Environment, Nuclear Technology Publishing, Vol. 45, No. 1-4, 1992.

KHADEMI A., ALEMI A.,A., NASSERI A.: *Transfer of radium of soil to plants in an area of high natural radioactivity in Ramsar, Iran.* Conference on Natural Radiation Environment III, US DOE Report CONF-780422, Bethseda, Maryland, 1980.

Rajaretnam G., Spitz, H.B.: *Effect of Leachability on Environmental Risk Assessment for Naturally Occurring Radioactivity Materials in Petroleum Oil Fields.* Health Physics, vol. 78 (2), 2000.

PEIC T., i inni: *Formation waters from oil and natural gas production: potential polluting source by Radium-226.* International Symposium on the Natural Radiation Environment (NRE-VI), w: Environment International, vol. 22, supl. 1, Pergamon Press 1996.

GUCAŁO L.K.: *Characteristics of radium distribution in underground waters of Dnieprowsko-Donieckoj Basin.* Gieochimja, vol. 12, 1964.

Dickson B. L.: *Evaluation of the Radioactive Anomalies Using Radium Isotopes in Groundwaters.* Journal of Geochemical Exploration, Vol. 19, 1966.

Gans I., i inni: *Radium in waste water from coal mines and other sources in FRG*. Second Symposium on Natural Radiation Environment, Bombay, India, Bethseda, DOE Symposium Series 1981.

Paschoa A.S., Nobrega A.W.: *Non-nuclear mining with radiological implications in Araxa*. International Conference On Radiation Hazards in Mining, Golden, Colorado, American Institute of Mining, Metallurgical, and Petroleum Engineers Inc., 1981.

Rogoż M., Posyłek E.: *Górnicze i geologiczne metody ograniczania zrzutów słonych wód z kopalń węgla kamiennego.* „Kierunki zagospodarowania zasolonych wód z kopalń węgla kamiennego", Główny Instytut Górnictwa, Katowice 1991.

Lebecka J., i inni: *Influence of Mining Activity on Distribution of Radium in the Natural Environment*. 4th Working Meeting Isotopes in Nature, Leipzig, Academy of Sciences of the GDR 1987.

Lebecka J., Skubacz K., Chałupnik S., Wysocka M.: *Skażenia promieniotwórcze środowiska naturalnego na Górnym Śląsku powodowane przez wody kopalniane i promieniotwórcze osady.*- Wiadomości Górnicze, no. 6, Katowice 1991.

Lebecka J., Chałupnik S., Wysocka M.: *Radioactivity of Mine Waters in Upper Silesian Coal Basin, and its Influence on Natural Environment.* 5th International Mine Water Congress, Nottingham, International Mine Water Association 1994.

Lebecka J., Chałupnik S., Śliwka M.: *Wyniki badań zachowania się radu podczas transportu słonych wód rurociągami (na przykładzie kolektora wód słonych OLZA).* Wiadomości Górnicze 5/92, Katowice 1992.

Tomza I., Lebecka J.: *Radium-bearing waters in coal mines: occurrence, methods of measurements and radiation hazard.* International Conference On Radiation Hazards in Mining, Golden, Colorado, American Institute of Mining, Metallurgical, and Petroleum Engineers Inc., 1981.

Ministerstwo Górnictwa i Energetyki: *Wytyczne kontroli skażeń promieniotwórczych środowiska naturalnego powodowanych przez kopalnie węgla kamiennego.* MGiE Katowice 1986.

Chałupnik S., Wysocka M.: *Wstępne wyniki oczyszczania wód dołowych z radu w KWK Piast, efekty I etapu wdrożenia.* Dokumentacja Głównego Instytutu Górnictwa, Katowice, 1999 (niepublikowane).

THEORETICAL STUDY OF RADIUM BEHAVIOUR IN AQUIFERS

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Abstract

In the paper, a theoretical approach to the problem of radium presence in mineralized mine water, is presented. Two main types of radium-bearing waters have been found in Polish coal mines. In type A waters, radium isotopes are present together with barium, while concentrations of sulphate ions are very low. Additionally, in these waters a ratio of ^{226}Ra:^{228}Ra activity is usually higher than 1. In type B waters, no barium can be fund, but radium together with sulphate ions. Contrary, in such waters the isotopic ratio of radium ^{226}Ra:^{228}Ra is below 1, and activities of both isotopes of radium are lower as in type A waters. No other differences in chemical composition of mine waters have been observed.

Analysis shows, that the activity ratio of radium isotopes is related to the dynamics of radium adsorption on the grains of solid phase in the aquifer. During analysis must be taken into account, that the radium build up in formation water due to recoil effect, is

stable in time. Additionally, no correlation with elevated concentrations of uranium and thorium in rocks, have been observed. Therefore the enhanced radium content in formation waters must be caused by its mineralization.

The relatively short half life of ^{228}Ra (6 years) shows, that the process of radium transfer from solid into liquid phase is a short term process for geological scale. Therefore radium content in mine waters must be related to the concentration of natural radionuclides in the close vicinity of the aquifer or the water reservoir.

Introduction

Enhanced levels of gamma radiation were discovered in Polish coal mines during the early 1960's by Saldan (1965) who concluded that this resulted from uranium mineralisation. More detailed investigations were initiated by Tomza & Lebecka [1981], and subsequently undertaken on a regular basis by the Laboratory of Radiometry in the Central Mining Institute, Katowice, Poland. Investigations are focused on the enhanced concentrations of radium isotopes in brines and in precipitates from radium-bearing waters. The results of the investigations show, that scales of barium and radium sulphates had been mis-identified as uranium mineralisation by Saldan[1965]. No elevated concentration of either uranium or thorium have been found in coal seams or the Carboniferous host rocks (Michalik et al., 1986; Wysocka and Skowronek, 1990] or in the brines [Pluta, 1988].

Similar phenomena in underground non-uranium mines in other countries have been described by other scientists. For instance in the Ruhr Basin, enhanced radium concentrations in brines were reported by Gans et. al. [1981]. Other investigators reported only the presence of barium in mine waters from coal mines, for instance Younger in the UK [1994] or Martel and co-workers in Canada [2001]. Reports of inflows of saline waters with elevated barium concentration came from a diamond mine in Russia [Kipko et al., 1994]. Based upon our experience [e.g. Lebecka et al., 1991] the presence of barium in mine water is likely to be correlated with enhanced radium concentration. High radium concentrations in formation waters from oil fields is widely, reported by scientists from USA, Romania, Ukraine or Norway [Tanner, 1964, Peic et al., 1995, Gucalo, 1964, Sidhu, 2002]. All these reports confirm the thesis, that the phenomenon of radium presence in brines is rather common, especially in confined aquifers, isolated from the influence of meteoric waters by impermeable layers, like clays or other deposits with low porosity [Tomza & Lebecka, 1981, Klessa, 2001] or even a thick permafrost layer.

In Polish coal mines two types of radium-bearing brines have been distinguished [Lebecka et. al., 1994]. The first type, called type A radium-bearing waters, contain radium and barium ions, but no sulphates. Type B waters, contain radium and sulphate ions but no barium. The presence of barium in brines is a very important factor controlling the behaviour of radium, because barium acts as a carrier. Therefore radium can be easily co-precipitated on barium from type A waters as scales of barium/radium sulphate. This chemical reaction leads to the formation of highly radioactive deposits in underground galleries and surface settling ponds and rivers. In type B brines no carrier for radium exist and the main processes, leading to the decrease of the concentration of radium isotopes are adsorption on bottom sediments in settling ponds and rivers and dilution. Radioactivity of sediments in the vicinity of mines, discharging B type radium-bearing waters into environment, is not very high but often clearly enhanced.

In table 1 typical chemical analyses of the two different radium-bearing brines are presented.

The results show little differences in the dissolved solids fractions of the two brines. The major difference is the absence of sulphate ions in type A and no barium in the B type water. Another significant difference is in the isotopic ratio of radium in both brines. Typically, in A type waters radium ^{226}Ra concentration is higher than the ^{228}Ra content – typically this ratio is about 2:1. In B type water the opposite can be seen - ^{226}Ra to ^{228}Ra ratio can be as low as 1:2 but sometime even 1:3.

The occurrence of radium-bearing waters in different coal mines in the Upper Silesian Coal Basin, the range of radium concentrations in brines, and its' influence on the natural environment have been investigated since the 70's and is well recognised. On the other hand, the origins and difference between the two types of is still a problem without adequate explanation.

Table 1. Comparison of chemical composition of brines A and B types.

	type A	type B
Conductivity 1S/cm	151000	91000
pH	7.25	7.53
TDS at 378K mg/dm^3	124300	85300
^{226}Ra Bq/dm^3	***62.76***	***3.449***
^{228}Ra Bq/dm^3	***34.67***	***5.10***
Cations		
Ca^{2+} mg/dm^3	6500	1840
Mg^{2+} mg/dm^3	3750	1980
Na^+ mg/dm^3	34720	28050
K^+ mg/dm^3	299	268
Fe mg/dm^3	60.05	60.05
Mn^{2+} mg/dm^3	60.05	60.05
Ba^{2+} mg/dm^3	1480	-
Total mg/dm^3	46740	32140
Anions		
Cl^- mg/dm^3	77350	50830
SO_4^{2-} mg/dm^3	0.0	2140
CO_3^{2-} mg/dm^3	0.0	0.0
HCO_3^- mg/dm^3	24.4	67.1
SiO_4^{4-} mg/dm^3	2.00	3.45
Br^- mg/dm^3	241	155
J^- mg/dm^3	10.9	11.2
Total mg/dm^3	77630	53210

Radium transfer and migration with water

The process of radium transfer from solid phase into water consists of three phases [Starik, 1964]:

- transfer of radium from the crystalline lattice into capillaries or pores in the mineral or rock, caused by the alpha-recoil effect resulting from the decay of parent nuclei, respectively ^{230}Th for ^{226}Ra; and ^{232}Th for ^{228}Ra;
- in pores an equilibrium between radium in solution and radium adsorbed on the surface of the mineral phase is established.

Starik furthermore stated that most of the radium seems to be adsorbed on surfaces;

- when mineral grains are in contact with flowing water, some of the radium may diffuse out of pores and capillaries (if a concentration gradient exists), but simultaneously part of radium can be desorbed from surfaces to balance the concentration.

Aqueous radium migration studies have been carried out by numerous scientists, but mainly for groundwater aquifers [Davidson & Dickson, 1986, Morse et. al., 2000, Benes, 1990]. One of the most important investigations has been performed by Krishnaswami and co-workers [1982] who assessed the adsorption/desorption ratio for radium and estimated the retardation factors for radium migration in the ground.

The simplified model of radium migration is based of the assumption of equilibrium between the concentration of radium in the liquid phase and that adsorbed on surfaces of solid phase [Frissel and Koster, 1990]. In this model the factor Kd describes the ratio of radium concentrations in solid and liquid phases according to:

$$K_d = Cs/Cw \qquad (1)$$

where:

Cs – concentration in solid phase [Bq/kg];

Cw – concentration in water [Bq/l]

This factor can be used to assess the migration velocity in the ground, which is defined as [Dickson, 1990]:

$$V_{Ra} = V_{H20}*/[1 + \rho K_d/\theta] \quad (2)$$

where:

Cs – concentration in solid phase;

Cw – concentration in water;

ρ - density of solid phase;

θ - moisture content of the ground;

V_{H20} – velocity of water movement in the aquifer (measured in m/year).

The radium movement in the aquifer is retarded significantly in comparison with water movement, and the retardation depends strongly on the Kd value.

During one half-life of ^{226}Ra (ca. 1600 y) the transport distance can be estimated as a maximum of several meters only. The effect of retardation is more important for ^{228}Ra due to its relatively short half-live - 6 years only. Within this period radium might be transported only several centimetres. It seems to be a certain limitation for the possible volume of the solid phase, influencing radium concentration in formation water.

However, the consideration of radium migration in aquifers is far more complex. Numerous data confirm [Nathwani and Phillips, 1979], that Kd values depend on the concentration of other ions in the liquid phase, and this makes it useless for analysis of radium transport in brines.

Another method that can be considered is based on the idea of cation exchange capacity – CEC. Cations in an aquifer compete for adsorption on a limited and stable number of adsorption centres, given by the CEC. This problem is relatively simple if only two types of cations are present in water. Otherwise, as in saline mine waters, several different cations can be found in the brine (see table 1). The analytical solution of such complex equations is very difficult, only a numerical approach is possible [Frissel and Reiniger, 1974]. The main limitation for this approach is that exchange factors are not stable, but depend on the total concentration of cations and chemical composition of dissolved solids.

The author would like to present a simple, mathematical approach to the problem of adsorption and desorption of radium in aquifers. The results for the simulation of changes in the radium isotopic concentration in water are compared with the results of long-term monitoring of radium content in different brines. That problem is not necessarily specific to the Silesian Basin, because reports of similar brines in different underground mines, especially non-uranium ones, and also in deep aquifers, are common.

One, additional issue is very important. One of the most important ions in brines is barium, which has very similar geochemical properties to radium. It seems that a most important problem would be to explain the presence of barium in some brines and absence in others. It is known, that barium is relatively easy dissolved by some hydrothermal fluids. For instance Krishnaswami and Turekian [1982] found in such fluids within basalts in Galapagos region a similar ratio of ^{226}Ra/Ba as in host rocks. Moreover, these scientists discovered similar values for this ratio in other volcanic areas. Of course, the mechanism of radium transfer into the liquid phase may be different, but the idea is supported by elevated barium contents in some saline waters.

Ion exchange kinetics:

Equations, describing the balance of radium in aquifers, are quoted from Dickson [1990]. Equation (3) presents changes of radium activity in the liquid phase and (4) on the surface of the solid phase.

For the liquid phase:

$$N_{rec} + k_2 {*} Ns = \lambda {*} Nw + k_1 {*} Nw \qquad (3)$$

For the solid phase:

$$k_1 Nw = \lambda {*} Ns + k_2 {*} Ns \qquad (4)$$

where:

N_{rec} – production of radium due to recoil effect;
k_1 – adsorption coefficient;
k_2 – desorption factor;
Nw – radium concentration in water;
Ns – radium content in solid phase.

The ratio of the radium atoms in the solution Nw to the transfer velocity into water, as a result of recoil Nrec, can be described as:

$$Nw/ N_{rec} = (\lambda+k_2)/(\lambda+ k_1+ k_2) \qquad (5)$$

Theoretically, the radium concentration in water could be calculated, taking into considerations measured or arbitrary chosen adsorption and desorption coefficients – different ones for A and B type of brines. During in-situ measurements parameters k_1 and k_2 must be measured for each aquifers. Data for in-situ investigations of these parameters are scare [Taskaev et al., 1978, Shangde et al, 2000]. Dickson [1972] showed, that measured values of adsorption/desorption coefficients often were not reliable. Therefore such an approach, based on the kinetics of ion exchange, may lead to wrong conclusions, if the above mentioned parameters are not well known.

It is proposed that a simplified, mathematical approach to this problem be used and the results compared with the actual results for Polish mines. One could consider this phenomenon as a product of the normal decay of the radionuclide (radium) in the liquid phase with additional exchange with solid surfaces (adsorption and desorption). Consider the Bateman equation for radium in the formation water in a modified form [Dickson, 1972], because only a part of radium atoms is transferred into water from solid phase. Assuming, that the recoil efficiency is denoted as e, the decay constant of the parent isotope (^{230}Th) is l and N is the number of parent isotope atoms in the volume unit, then the number of radium atoms, recoiling into liquid phase, can be calculated as:

$$N_{rec} = N * \lambda * \varepsilon = A * \varepsilon \qquad (6)$$

Consider first the case of simple decay with possible adsorption, while desorption is omitted [Semkow et al., 1996]. On such an assumption, the equation, describing changes in the radium content in the liquid phase, as follows:

$$dN_{Ra}/dt = N_{rec} - \lambda * N_{Ra} - k_1 * N_{Ra} \qquad (7)$$

When desorption is also taken into account along with another assumption; that the number of atoms in the liquid phase is similar to those adsorbed on solid surfaces, the final formula is different:

$$dN_{Ra}/dt = N_{rec} - \lambda * N_{Ra} - k_1 * N_{Ra} + k_2 * N_{Ra} \qquad (7a)$$

where:

$\lambda * N_{Ra}$ – this part describes the radioactive decay of radium in the solution, λ is the decay constant of radium and N_{Ra} is numer of radium atoms in liquid phase;

$k_1 * N_{Ra}$ – the adsorption on the solid phase, k_1 is the adsorption coefficient;

$k_2 * N_{Ra}$ – the desorption into liquid phase, k_2 is the desorption coefficient.

The solution of equation (8) is:

$$N_{Ra}(t) = N_{rec}/(\lambda+k_1)*(1-\exp[-(\lambda+k_1)*t]) \qquad (8)$$

or, for the case with desorption:

$$N_{Ra}(t) = N_{rec}/(\lambda+k_1-k_2)*(1-\exp[-(\lambda+k_1-k_2)*t]) \qquad (8a)$$

Some conclusions can be drawn from these equations. Firstly, the dynamic equilibrium in the liquid phase seems to depend mainly on adsorption and desorption rates. The main reason is that decay the constants of ^{226}Ra and ^{228}Ra isotopes are much lower than the adsorption/desorption coefficients. The decay constant of ^{228}Ra is $3.7*10^{-9}$ s^{-1} only and l for ^{226}Ra is even lower, while the estimate of the adsorption rate for groundwaters gave values within the range 0.5 -10^{-6} s^{-1} [Dickson, 1990]. It means, that the equilibrium level of radium in the liquid phase should be controlled by other processes, not the decay. On the other hand, the adsorption and desorption rates of radium must depend on the solutes in the formation water and especially the presence of barium ions.

From the above equations it is clear that adsorption and desorption processes affect the level of radium concentration in liquid phase. The ratio of equilibrium concentrations for cases without and with adsorption/desorption is $1/((+k_1-k_2)$. Taking into consideration the assumption, that k_1-k_2 » l, the activity ratio is about $1/(k_1-k_2)$. This effect should be more important for the isotope with the lower decay constant - ^{226}Ra. Although usually concentrations of radionuclides from uranium and thorium series in the solid phase are similar, the situation in the liquid phase should be different. If adsorption and desorption rates for both isotopes are the same, than the activity ratio in the solution should be $A^{226}/A^{228} = 6/1600 \approx 0.004$. Such low ratios are not usually observed in aquifers, if at all. It means, that another explanation is required.

Radium in mine waters

Any theory must explain the observed different effects found in brines in coal mines. As mentioned earlier, the ratio of radium concentrations in A type brines

(^{226}Ra/^{228}Ra) is higher than 1. It might be explained as a combination of the low adsorption rate, resulting in longer time needed to reach equilibrium in the liquid phase, and the higher concentrations of radium in A type waters.

In B type waters the lack of barium leads to the higher adsorption rate and slower desorption. The main effect is that there is a shorter time required to reach equilibrium in the liquid phase. Additionally, the activity ratio ^{226}Ra: ^{228}Ra should be below 1, as observed.

Assuming that recoil is the only mechanism of radium transfer into the liquid phase and that no adsorption occurs, the build up of activity can be described as:

$$A_{Ra}(t) = (N_{rec}/\lambda)*(1-\exp[-\lambda*t]) = (A*\varepsilon/\lambda)*(1-\exp[-\lambda*t]) \qquad (9)$$

where N_{rec}/λ is the maximum activity of radium in water.

By considering the following parameters for the host rock in the aquifer: – the concentrations of uranium and thorium isotopes are each 25 Bq/kg, the density of the rocks is 2000 kg/m^3, the recoil coefficient e»10% [Semkov et al., 1998], and a porosity of 10 %, than the calculated maximum radium activity in the liquid phase should be 50 kBq/m^3. However in Polish coal mines, much higher values have been measured, up to 400 kBq/m^3 [Lebecka et. al., 1993]. It is understandable, because often concentrations of radionuclides in rock body are higher, up to 200 Bq/kg. The fact, that the radium ^{226}Ra concentrations are higher than those of ^{228}Ra has been explained by Dickson [Dickson, 1990] to be the result of the previously mentioned recoil and adsorption of 230Th on the surface of solid phase. It is possible that the recoil dissolution of ^{226}Ra may be more effective than ^{228}Ra, since the parent 232Th is probably entirely embedded in the lattice. It is necessary to stress again, that such high radium concentrations in water are not connected with uranium or thorium mineralization.

Comparing equation (9) for the two isotopes of radium, ^{226}Ra from the uranium series and ^{228}Ra from thorium chain, and making the assumption that the recoil coefficient is similar for both radionuclides and that no adsorption occurs, the ratio of their activities in the liquid phase is as follows:

$$A_{226}/A_{228} = (\lambda_{228}/\lambda_{226})A_U*\{1-\exp[-\lambda_{226}*t]\}/ A_{Th}* \{1-\exp[-\lambda_{228}*t]\} \qquad (10)$$

Taking into account the adsorption and desorption (equation 8a), the activity ratio can be denoted as:

$$A_{226}/A_{228} = (A_U/A_{Th}) * \{\lambda_{228}/(\lambda_{226}+k_1-k_2) * (1-\exp[-(\lambda_{226}+k_1-k_2)*t])\} / \{\lambda_{226}/(\lambda_{228}+k_1-k_2) * (1-\exp[-(\lambda_{228}+k_1-k_2)*t])\} \qquad (11)$$

If the adsorption coefficient is significantly higher than the decay constant of both radium isotopes, then equation (11) can be simplified further (taking into account a longer time for water contact with the solid phase):

$$A_{226}/A_{228} = (A_U/A_{Th}) * \{\lambda_{228}/(\lambda_{226}+k_1-k_2)\} / \{\lambda_{226}/(\lambda_{228}+k_1-k_2)\} \qquad (12)$$

If we assume a much higher value for the adsorption coefficient in comparison with desorption, a final equation is simpler:

$$A_{226}/A_{228} = (A_U/A_{Th})(\lambda_{228}/\lambda_{226}) \qquad (13)$$

The conclusion from the last equation is important. Such a big difference of activity ratio is not observed in mine waters. It means that adsorption and desorption coefficients in saline water aquifers are similar, rather low and comparable with the decay constants of radium isotopes. Therefore the equation (13) cannot be used for the prediction of radium concentrations in brines.

The use of the concept of an effective adsorption coefficient keff, obtained from the subtraction of adsorption and desorption factors ($k_{eff} = k_1 - k_2$), for numerical simulation of the build-up of radium isotope concentrations in the liquid phase in aquifer is proposed. Such simulation has been made for different values of effective adsorption coefficients and results are presented in table 2. The activities (concentrations) of radium isotopes are relative values and have been normalised to enable comparison of the increase of these values with time. The uranium:thorium ratio in the solid phase has been chosen as 1, which is close to actuality.

Table 2a. Results of simulation of activity ratio of radium isotopes in the liquid phase for different values of effective adsorption coefficient.

Time	k_{eff} = 0 [s^{-1}]			k_{eff} = 1,4*10^{-11} [s^{-1}]		
[years]	A_{226}	A_{228}	A_{226}/ A_{228}	A_{226}	A_{228}	A_{226}/ A_{228}
1	0,000437	0,110118	0,003972	0,000437	0,110095	0,003972
5	0,002185	0,441965	0,004944	0,002183	0,441528	0,004944
10	0,004365	0,688597	0,00634	0,004356	0,687379	0,006337
50	0,021637	0,997072	0,021701	0,021403	0,99341	0,021545
100	0,042807	0,999991	0,042807	0,041891	0,996256	0,042048
500	0,196477	1	0,196477	0,177176	0,996264	0,17784
1000	0,354351	1	0,354351	0,291569	0,996264	0,292662
5000	0,887803	1	0,887803	0,493706	0,996264	0,495557
10000	0,987412	1	0,987412	0,499921	0,996264	0,501795

Table 2b. Results of simulation of activity ratio of radium isotopes in the liquid phase for different values of effective adsorption coefficient.

Time	k_{eff} = 1,4*10^{-10} [s^{-1}]			k_{eff} = 3,7*10^{-09} [s^{-1}]		
[years]	A_{226}	A_{228}	A_{226}/ A_{228}	A_{226}	A_{228}	A_{226}/ A_{228}
1	0,000436	0,109882	0,003972	0,000413	0,104049	0,003968
5	0,002161	0,437628	0,004939	0,001655	0,344205	0,004809
10	0,004271	0,676556	0,006313	0,002576	0,451321	0,005708
50	0,019442	0,961588	0,020219	0,003721	0,49971	0,007447
100	0,034726	0,96385	0,036029	0,003732	0,499714	0,007468
500	0,082713	0,963855	0,085815	0,003732	0,499714	0,007468
1000	0,09017	0,963855	0,093552	0,003732	0,499714	0,007468
5000	0,090909	0,963855	0,094318	0,003732	0,499714	0,007468
10000	0,090909	0,963855	0,094318	0,003732	0,499714	0,007468

The results of these approximate estimations seems to be a little surprising. First of all – the effective adsorption of radium from brines is a very slow process. For A type waters value of this coefficient must be close to zero and adsorption simply does not occur. The activity ratio ^{226}Ra:^{228}Ra is of about 1, equal to the chosen activity ratio in the solid phase. The observed higher values, up to 2, can be explained, accordingly to Dickson [Dickson, 1990], by the higher recoil rate for ^{226}Ra as a result of a previous recoil of parent isotope ^{230}Th. The recoil ratio of radium isotopes has been calculated by Dickson as 2:1 and this value is in a good agreement with experimental data.

For the effective adsorption coefficient, equal to the decay constant of ^{226}Ra (keff = 1,4*10^{-11} s^{-1}), the activity ratio was calculated above as 1:2, and this is close to the activity ratio measured for B type waters. In such waters the adsorption prevails over desorption, but the process appears to be very slow. The reason is that the presence of sodium and calcium ions in the liquid phase, compete with radium ions for the CECs.

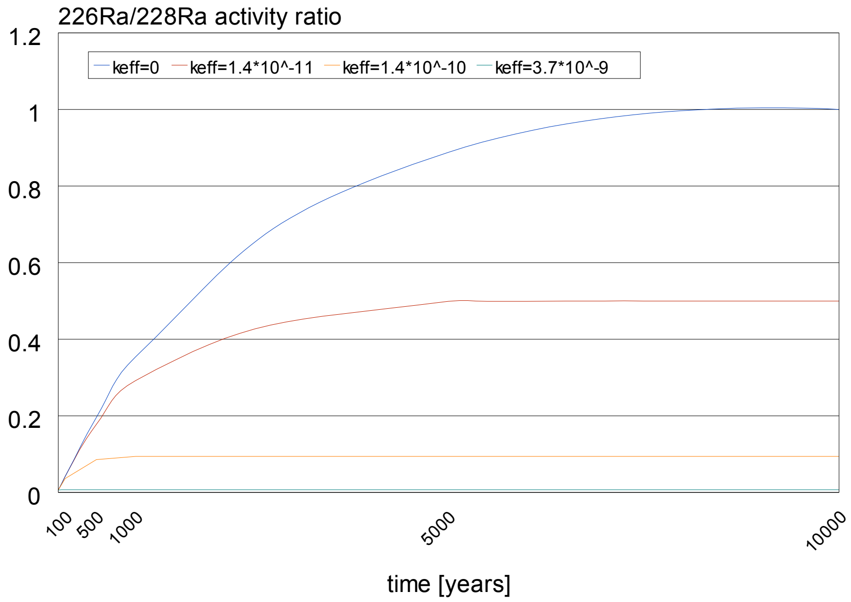

Fig.1. Simulation of the activity ratio of radium isotopes in brines for different effective adsoption coefficients

Higher values of effective adsorption coefficient seem to be too high for aquifers with saline waters. For instance, the activity ratio, calculated for the keff =1,4*10^{-11} s^{-1}, corresponding to period of 160 years (1/10th of ^{226}Ra half-life), give the value of activity ratio = 0.1. In Polish coal mines such an activity ratio has not been observed. Again, this conclusion supports strongly the thesis that the ionic exchange of radium with solid phase is an extremely slow process.

On the other hand, we have to remember, that all conclusions are related to the effective adsorption coefficient, which describes the difference between adsorption and desorption. Physically, both processes are fast and there have been numerous investigations on this subject, each giving clear evidence that desorption could take place within hours or even minutes [Chalupnik, 2003].

The problem needs further analyses and in-situ measurements to investigate brines and deep aquifers. One of the best possible sites is a colliery in southern part of Upper Silesian Coal Basin, where both types of radium bearing brines are present.

Summary

An approach to the problem of radium transfer from solid into liquid phase in aquifers is described in the paper, with special emphasis to brines that occur in coal mines. The main process, controlling the radium concentration in water, is adsorption of radium on the surfaces of solid phase. However the adsorption coefficient strongly depends on the dissolved solid content of the brines, and primarily on the barium presence in saline waters.

The migration length of radium isotopes in an aquifer is rather short, several meters for ^{226}Ra and less than 1 meter for ^{228}Ra. Therefore investigations of the stratum in the close vicinity of mine galleries should give important information of the uranium and thorium content in the solid phase as well as other parameters of the aquifer such as porosity, Eh, pH etc. All these results will be essential for the further investigations of radium behaviour in deep aquifers.

The results of simulation, based on the mathematical approach to the radium changes in the liquid phase, revealed that effective adsorption rate of radium from brines is very low, either comparable with the decay constant of ^{226}Ra or even lower. Differences of adsorption coefficient, mainly due to the presence of barium ions in A type brines, lead to the significant differences in the activity ratio of radium isotopes. It means, that one of the most important features is the reason for barium occurrence in some aquifers. From that point of view, the changes in radium concentration is a secondary problem.

Further research is required, mainly in-situ experiments directly within aquifers. The best possible sites seem to be deep underground mines, like collieries, with easy access to different aquifers. In one of coal mines in Poland both types of radium-bearing waters are present (A & B), therefore we would like to use this mine during future investigations.

References

Benes P. – *Radium in continental surface water* - Technical Report “The environmental behaviour of radium”, IAEA, Vienna, STI/DOC/10/310, 1990.

Centeno L., et.al., – *Radium-226 in coal-mine effluent, Perry County, Ohio* – Proc. of Geological Society of America Annual Meeting, Boston, 2001.

Chałupnik S. – *Purification of mine water of radium* – IAEA-Tecodc-1271, Vienna 2002.

Chałupnik S. – *Investigation of radium leaching from mine sediments* – Kwartalnik Głównego Instytutu Górnictwa, no.3, 2003 (in Polish).

Davidson M.R., Dickson B.L. – *A porous flow model for steady-state transport of radium in groundwater* - Water Resources Journal, vol.22, 1986.

de Jezus A.S.M. - *Behaviour of Radium In Waterways and Aquifers* – IAEA Tecdoc 301, Vienna 1984.

Dickson B. L., et.al., - *Evaluation of the Radioactive Anomalies Using* ^{226}Radium *Isotopes in Groundwaters* - J. of Geochemical Exploration, Vol. 19, 1972.

Dickson B.L. – *Radium in groundwater* - Technical Report "The environmental behaviour of radium", IAEA, Vienna, STI/DOC/10/310, 1990.

Dickson B.L. – *Radium isotopes in saline seepages, south-western Yilgarn, Western Australia* – Geochimica and Cosmochemica Acta, vol. 49, 1985.

Frissel M.J., Koster H.W. – *Radium in soil* - Technical Report "The environmental behaviour of radium", IAEA, Vienna, STI/DOC/10/310, 1990.

Frissel M.J., Reiniger P. – *Simulation of accumulation and leaching in soils* – PUDOC, Wageningen, Netherlands, 1974.

Sidhu R. – *Radium in formation waters from oil fields in Norway* – Int. Conference ENOR III, Dresden 2003, (in press).

Gans I., et.al., - *Radium in waste water from coal mines and other sources in FRG* - Second Symposium on Natural Radiation Environment, Bombay, India, 1981.

Gucalo L.K. - *O niekotorych zakonomiernostiach raspredielenija radia w podziemnych wodach sredniej czasti Dnieprowsko-Donieckoj Wpadliny* - Gieochimja, vol. 12, 1964.

Humphreys, C.L. - *Factors controlling uranium and radium isotopic distributions in groundwaters of the west-central Florida phosphate district*. - In Graves, B., ed. Radon, Radium and other Radioactivity in Groundwaters, Lewis Publishers, 1987.

Kipko E.Y., et.al. – *Environmental Projection during mining of diamond deposits of Yakutiya* – Proc. Of 5th Int. Mine Water Congress, Quorn Repro Ltd., Loughgorough, England, 1994.

Klessa D. – *Availabilities of radionuclides and non-radiological contaminants in sediments* - Mine Water and the Environment, Uniwersytet Śląski, Katowice, 2001.

Koster H.W., et.al. - *^{210}Po, ^{210}Pb,* ^{226}Ra *in Aquatic Ecosystems and Polders, Anthropogenic Sources, Distribution and Enhanced Radiation Doses in the Netherlands* - The Natual Radiation Environment, Nuclear Technology Publishing, Vol. 45, Nos. 1-4, (1992).

Kraemer T.F., Reid D.F. – *The occurrence and behaviour of radium in saline formation water of the U.S. Gulf Coast region* – Isotope Geoscience, vol. 2, 1984.

Krishnaswami S., et.al. – *Radium, thorium and radioactive lead isotopes in groundwater* – Water Resources Research, vol. 18, 1982.

Krishnaswami S., Turekian K.K. – *U-238, Ra-226 and Pb-210 in some vent waters of the Galapagos spreading center* – Geophysical Research Letters, vol. 9, 1982.

Langmuir D., Riese A.C. – *The thermodynamic properties of radium* – Geochemical and Cosmochemical Acta, vol. 49, 1985.

Lebecka J. et.al. - *Radioactive contamination of Upper Silesia as a result of release of brines and deposits from coal mines* - Wiadomości Górnicze, 6/91, Katowice 1991 (in Polish).

Lebecka J., et.al - *Influence of Mining Activity on Distribution of Radium in the Natural Environment* - Proc. of 4th Working Meeting Isotopes in Nature, Leipzig, 1986.

Lebecka J., et.al. - *Methods of Monitoring of Radiation Exposure in Polish Coal Mines* - Nukleonika Vol 38, 1993.

Martel A.T., et.al. - *Brines in the Carboniferous Sydney Coalfield, Northern Canada* – Applied Geochemistry, vol. 16, 2001.

Martin R., Akber R.A.– *Radium isotopes as indicator of adsorption-desorption interactions and barite formation in groundwater* – J. of Environmental Radioactivity, vol. 46, 1999.

Michalik B., Chałupnik S., Skowronek J. – *Występowanie naturalnych izotopów promieniotwórczych w węglach na terenie GZW - metodyka i wstępne wyniki badań* – Zeszyty Naukowe Politechniki Śląskiej, Seria : Górnictwo, z. 149, Gliwice 1986.

Moise T., et.al. – *Ra isotopes and Rn in brines and groundwaters of the Jordan-Dead Sea Rift Valley: enrichment, retardation and mixing* – Geochemica and Cosmochemica Acta, vol. 64, 2000.

Nathwani J.S., Phillips C.R. - *Adsorption of Ra-226 by soils in the presence of Ca^{2+} ions* – Chemosphere, vol. 5, 1979

Paridaens J., Vanmarcke H – *Radium contamination of the Laak rivers bank as a consequence of phosphate industry in Belgium* – IAEA-Tecdoc-1271, Vienna 2002.

Paschoa A.S., Nobrega A.W. - *Non-nuclear mining with radiological implications in Araxa* - Int. Conf. On Radiation Hazards in Mining, Golden, Co, 1981.

Peic T., et.al. - *Formation waters from oil and natural gas production: potential polluting source by Radium-226* - International Symposium on the Natural Radiation Environment (NRE-VI), Montreal, 1995.

Pluta I. – *Uranium in waters from Carboniferous aquifers in southern part of USCB* – Zeszyty Naukowe Politechniki Śląskiej, seria Górnictwo, z. 172, 1988 (in Polish).

Pluta I., Zuber A. – *Uranium and radium-226 and origin of brines in Upper Silesian Coal Basin* – Prace Naukowe Instytuttu Geotechniki Politechniki Wrocławskiej, nr. 58, 1989 (in Polish).

Sałdan M. – *Uranium origin in Carboniferous strata in USCB* - Biuletyn Instytutu Geologicznego, Warszawa, vol. 5, 1965 (in Polish).

Shangde L., et.al. – *In-situ radionuclide transport and preferential groundwater flow at Idaho* – Geochemica and Cosmochemica Acta, vol. 65, 2000.

Starik I.E. – *Principles of Radiochemistry* – U.S. Atomic Energy Commission Report, AEC-tr-6314, 1964.

Tanner A.B. – *Radium migration In the ground: a review* – Natural Radiation Environment Conference, University of Chicago Press, Chicago, 1964.

Taskayev A. I., et al. – *Forms of radium-226 in soil horizons containing its high concentrations* – Pochvovedenie, vol. 2, 1978.

Tomza I., Lebecka J., - *Radium-bearing waters in coal mines: occurrence, methods of measurements and radiation hazard* - Int. Conf. On Radiation Hazards in Mining, Golden, Co, 1981.

Wysocka M. et.al. – *Radium in mine waters in Poland: occurrence and impact on rivers* – International Conference “Ecological Aspects of Coal Mining”, Katowice, 1997.

Wysocka M., Skowronek J. - *Analysis of natural radioactivity of coals from Upper Silesian Basin in aspects of geological structure* - Int. Symp. On Nuclear techniques in the Exploration and Exploitation of Energy and mineral resources. IAEA-SM-308 Vienna, IAEA 1990.

Younger P.L., et.al. – *Application of geochemical mineral exploitation techniques to the cataloguing of discharges from abandoned mines in north east England* - Proc. Of 5th Int. Mine Water Congress, Quorn Repro Ltd., Loughgorough, England, 1994.

RADIUM BEHAVIOUR DURING DESALINATION PROCESSES OF MINE WATERS

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Abstract

In 80's and 90's investigations of radium behaviour in desalination plant have been performed by Laboratory of Radiometry of the Central Mining Institute. Thisplant has been located in Dębieńsko Mine for complete removal of dissolved solids from mineralized mine waters. The installation was a very unique solution, the only one constructed for such purposes in Poland and all over the world. In the plant brines from two coal mines have been treated. These salty waters were additionally radium bearing ones, containing enhanced levels of radium isotopes (Ra-226 and Ra-228). Our investigation showed enhanced concentrations of radium in different waste materials and by-products of the process. Therefore the economical use of such products wasn't possible.

In last years a plan of the construction of the desalination plant for another group of mines was under the discussion (Piast and Ziemowit Collieries). Results of investigations of contamination of the natural environment, caused by radium-bearing waters from these mines, indicated how severe this problem was. To solve this influence, the removal of radium in underground galleries has been applied in one of these mines.

On the basis of previous investigations in Dębieńsko Desalination Plant, an analysis of radium behaviour in planned installation has been prepared. It was done for two possible scenarios – without and with radium removal from mine waters, preceded the desalination process. Results of the analysis are presented in the paper. This assessment gives a very good opportunity to point out how important may be radium removal from mine waters – not only to minimize environmental pollution but also to enable utilization of certain products of desalination process.

1. Introduction

Saline waters, discharged from coal mines in Upper Silesia region often cause significant pollution of the small brooks and rivers in their vicinity. It is due to high mineralization, sometimes up to 200 g/dm^3. Such waters also contain natural radionuclides, mainly radium isotopes. It is difficult to control a negative impact of salinity on the surface waters, only few methods are possible to apply. One of the possible methods is desalination. In 70's the desalination plant has been built for removal of salinity from brines of two coal mines in Poland. The construction of the plant was supported by United Nations within UNDP programme.

This plant has been located in Dębieńsko Mine for complete removal of dissolved solids from medium mineralized mine waters. The installation was a very unique solution, the only one constructed for such purposes in Poland and all over the world. In the plant brines from two coal mines have been treated. These salty waters were additionally radium bearing ones, containing enhanced levels of radium isotopes (^{226}Ra and ^{228}Ra). In this plant B type waters were treated in two separate installation.

Primary installation was used to concentrate salts by evaporation, during this process sodium chloride was produced (useful for consumption), gypsum as a waste product, deionised water and a liquid by-product. This saturated solution of different salts has been transferred into secondary installation to be utilized for production of iodine and bromine, potassium chloride, magnesium hydroxide and deionised water. No waste were produced in this installation.

In 80's and 90's investigations of radium behaviour in desalination plant have been performed by Laboratory of Radiometry of the Central Mining Institute. We investigated concentration of radium isotopes in different products and by-products of the primary and secondary installations. It has been found, that different products of the desalination contained enhanced concentrations of radium. Moreover, presence of scales with high radium content inside the primary installation has been confirmed by gamma dose rate measurements. It should be pointed out that brines, demineralized in this plant, weren't very salty and didn't contain high radium concentrations, for instance ^{226}Ra concentration was up to 1.5 kBq/m^3 and ^{228}Ra level reached 3 kBq/m^3, while the salinity wass up to 30 g/dm^3.

At the end of 90's a feasibility study of new desalination plant has been prepared for three collieries in the Vistula catchment area, where huge inflows of highly mineralized brines occur (Central Desalination Plant – CDP). These waters were also B type brines but concentrations of radium isotopes were significantly higher – up to 7 kBq/m^3 of ^{228}Ra and 15 kBq/m^3 of ^{228}Ra. Direct desalination of these brines could lead to the creation of products and by-products with much higher levels of radionuclides as in the existing plant. Additionally, we could predict deposition of scales with enhanced levels of radium in evaporation units or reverse osmosis units, and the gamma dose rates near particular parts of primary installation may increase radiation hazard for workers above the level 1 mSv/year. The way to avoid it would be a radium purification of mine water prior to desalination. An assessment of the radium levels in different products of desalination has been prepared for two scenarios. The first one for desalination of untreated brines and the second for the demineralization of brines, previously purified of radium.

2. Primary desalination system

The main aim of the primary installation was to concentrate the brine in the evaporation or reverse osmosis processes (during this stage distilled water was produced), then to separate gypsum and sodium chloride. Remains of the concentrated brine were transferred into the secondary system. Majority of radium activity has been removed from the solution with gypsum – of about 60% of initial activity. Small quantities of radium can be found in the NaCl but only in admixtures of poorly separated gypsum. Additionally in the primary system scales of gypsum (CaSO4), barium and radium sulphates were deposited in some parts of evaporating units and salt crystallizer. These scales contained high concentration of radium isotopes – up to few tens of kBq/kg. The fraction of radium total activity in scales is very low, nonetheless its deposition led to significant increase of gamma dose rates in particular parts of the system and possible hazard for workers. Also significant fraction of radium remained in the concentrated brine and caused contamination of the products in the secondary installation. No radium has been found in distilled water, and this is a very important for possible use of water as potable water.

I. Radium isotopes in gypsum.

Several samples of gypsum from the system have been measured by gamma spectrometry. It was found that average concentration of ^{226}Ra was of about 60 Bq/kg, while maximum value didn't exceed 100 Bq/kg. Accordingly to the Instruction No 234 of Institute of Construction Techniques, for construction of dwellings materials with concentration of radium ^{226}Ra below 185 Bq/kg can be used. Secondary condition for the total activity of natural radionuclides in the material is as follows:

$0.00027 \cdot C_K + 0.0027 \cdot C_{Ra} + 0.0043 \cdot C_{Th} < 1$

where:

C_K, C_{Ra} and C_{Th} – concentrations of ^{40}K, ^{226}Ra i ^{228}Ra.

Also this second requirement was fullfiled for gypsum by-product from the primary installation.

For the planned installation results of the assessment are shown in table 1:

Table 1. Predicted concentration of radium isotopes in gypsum

	Without prification	**After radium removal from brines**
^{226}Ra [Bq/kg]	400	10
^{228}Ra [Bq/kg]	800	20
Possibility of application	Waste with enhanced radium content – no application	Can be used in the construction industry

It can be clearly seen, that only in case, when prior the desalination brines would be purified of radium, gypsum from primary installation of CDP would be used for construction purposes.

II. Radium in sodium chloride NaCl.

Presence of radium isotopes in sodium chloride was due to poor separation of gypsum at the first stage of primary system. It has been found, that gypsum fraction in the salt varied in a wide range, affecting radium content in this product. Maximum value of ^{226}Ra concentration was 7 Bq/kg, while ^{228}Ra was slightly higher – up to 10 Bq/kg. Therefore it is difficult to predict radium concentration in sodium chloride in the

CDP installation. Taking into account, that similar fraction of gypsum might be present in sodium chloride, very rough assessment of radium isotopes concentration is done (see table 2).

Table 2. Predicted values of radium concentrations in NaCl

	Without prification	**After radium removal from brines**
^{226}Ra [Bq/kg]	40	1
^{228}Ra [Bq/kg]	80	2
Possibility of application	Can be used for consumption with restrictions	Can be used for consumption

In both cases NaCl, produced in CDP, could be used for the consumption. But in the case of no purification of brines before desalination an effective dose for people must be estimated. Taking into account the use of 1 kg/year of salt, total ingested activity of radium isotopes is 120 Bq and annual dose would be close to 0.1 mSv. Due to Euratom/96/ Directive this is a permissible level of additional dose caused by radionuclides in drinking water (10% of annual dose 1 mSv). Therefore some restrictions must be applied for the use of salt from CDP as well as requirement of periodic monitoring of radium level in NaCl.

III. Scales in the primary installation.

The presence of scale with enhanced radium content has been discovered during measurements of gamma dose rate at the primary installation. The highest value of gamma dose rate has been measured in the vicinity of heat exchangers of evaporation units. In scales taken from these exchangers radium ^{226}Ra content was up to 10 kBq/kg, while maximum values of gamma dose rate varied from 3 to 5 μGy/h on the surfaces of pipes and as high as 1 μGy/h at the distance 1 m away.

In this case the assessment of radium concentrations in scale is difficult. One of the reasons is the fact, that radium content in scales in controlled not only by radium concentration in brines but also depends on the abundance of radium sulphate in calcim sulphate (gypsum). The assumption can be made that radium concentration in scales of CDP would be similar or slightly higher as measured in Dębieńsko desalination plant, if no purification of brines will be applied. So estimated values of radium content are 10-20 kBq/kg for ^{226}Ra and 20-40 kBq/kg for ^{228}Ra. But total activity of radium in scales would be correlated with radium concentration in raw brine and with the total mass of scales in the installation. Gamma dose rate values would depend, of course, on the total activity of radium isotopes in scales. We should predict the increase of gamma dose rates during the exploitation of the CDP, but maximum values would be similar to values, measured in Dębieńsko plant. **It must be taken into account, that concentration of radium isotopes in scales would be higher as 10 kBq/kg and such scales must be treated as waste products with enhanced natural radioactivity.** In such case special measures must be undertaken during any repairs at the primary installation of CDP or scales removal from pipes. This problem may appear after few years of CDP exploitation.

3. Secondary desalination system

In the secondary system of Dębieńsko desalination plant iodine, bromine, potassium chloride (KCl), magnesium hydroxide and calcium chloride were produced. Saturated brines from primary installation were utilized in this system, radium concentrations in these branes were up to 10 times higher in comparison with raw brines. In saturated brines in secondary system of Dębieńsko plant ^{226}Ra concentration reached sometimes value 15 kBq/m^3, while radium content in raw brine was in average 1.5 kBq/m^3. As no waste or by-products were created in the secondary installation, therefore 30-40% of total radium activity from raw brine were distributed in different products of that system. The similar situation would be observed in CDP.

I. Iodine and bromine solutions.

Radium concentration is solutions, containing iodine and bromine have been measured several time in Dębieńsko. No radium (above detection limit) has been found in these samples. We can assume the same situation in CDP, so no contamination of these products is predicted.

II. Potassium chloride (KCl)

In karnalite not only radium isotopes were found but mainly the natural radionuclide of potassium - ^{40}K. It's abundance in natural postassium is a constant value, despite the origin of KCl. The presence of ^{40}K in potassium chloride is a possible source of radiation hazard for workers, as it's concentration in the material is of about 15 kBq/kg. This isotope may cause the increase of external dose of gamma radiation.

Radium isotopes could appear in the karnalite as a result of a poor separation of gypsum. Maximum value of ^{226}Ra concentration in potassium chloride from Dębieńsko plant was as high as 300 Bq/kg, but the average concentration was much lower - 70 Bq/kg. For CDP the most important factor, influencing radium content in this product would be proper technology and maintenance of the system. Results of rough assessment of radium isotopes concentration in karnalite from CDP are shown in table 3.

Table 3. Predicted concentration of radium isotopes in KCl

	Without prification	**After radium removal from brines**
^{226}Ra [Bq/kg]	1200	30
^{228}Ra [Bq/kg]	2400	60
Possibility of application	Limited application as the fertilizer	No restriction of use

It can be seen, that after the purification of mine waters before desalination, potassium chloride can be used without any restriction for all possible applications.

III. Magnesium hydroxide.

In the Dębieńsko desalination plant one of the products in the secondary installation was magnesium chloride. No radium ^{226}Ra has been found in samples of this product, therefore no restriction of use were applied.

In the CDP installation instead of magnesium chloride, magnesium hydroxide was proposed to be produced. Therefore for the assessment of radium content in this product another approach must be applied. An analogy can be drawn from results of investigations of another desalination installation, designed and built as a model one at Ziemowit Mine by Silesian Technical University [21]. We found, that radium content ^{226}Ra in samples of magnesium hydroxide from this installation didn't exceed 25 Bq/kg. Results of the assessment are shown in table 4, such product can be used without restriction for any application.

Table 4. Predicted concentration of radium isotopes in magnesium hydroxide.

	Without prification	**After radium removal from brines**
^{226}Ra [Bq/kg]	25	3
^{228}Ra [Bq/kg]	50	6
Possibility of application	Use without restrictions	Use without restrictions

Additional by-product at this stage of process are traces of gypsum from the primary system. It's difficult to assess the radium concentration in this by-product as in Dębieńsko desalination plant only small amounts of gypsum were obtained from secondary system. Concentrations up to 1 kBq/kg of ^{226}Ra have been measured. Therefore it would be possible to produce in CDP gypsum with ^{226}Ra content up to several kBq/kg and 10 kBq/kg of ^{228}Ra. Such by-product must be treated as a waste with enhanced content of natural radionuclides, but these small amounts of gypsum could be mixed with low active gypsum from primary installation.

IV. Calcium chloride.

Last stage of the proposed desalination process is separation of calcium chloride. In the Debieńsko desalination plant as well as in the mdel installation at Ziemowit mine this element of the process didn't exist. Only analogous process was production of calcium carbonate in Ziemowit installation. This similarity is not adequate as radium in a form of carbonate is insoluble while in a form of chloride is soluble. Therefore radium behaviour in both cases might be different. Taking into account a certain similarity of both processes (in case of Ziemowit installation radium concentration in calcium carbonate varied between 800 up to 2000 Bq/kg), an assumption results are shown in table 5.

Table 5. Predicted radium content in calcium chloride.

	Without prification	**After radium removal from brines**
^{226}Ra [Bq/kg]	2000	80
^{228}Ra [Bq/kg]	4000	160
Possibility of application	Very limited use	Use without restrictions

It must be pointed out, that this stage of the planned process is not known very well and in case of implementation of the technology in practise must be investigated very carefully.

Very important conclusion of long term monitoring of radium isotopes in distilled water is following. Concentrations of ^{226}Ra and ^{228}Ra in water produced in Debieńsko desalination plant were close to zero, usually below detection limit.

4. Radiological hazard due to the desalination of mine waters.

Desalination plant might be a possible source of radioactive contamination for the environment only in case, when desalination of untreated mine waters would be performed. Under such circumstances radium concentration could exceed permissible levels in particular products of the process. Basic product of the process – distilled water – can be used for the consumption without any restriction. Slightly more complicated problem would be the use of NaCl, but also in this case consumption seems to be possible, especially when proper and carefull maintanance of the plant is ensured.

Rather complicated can be the status of other products due to enhanced radium content. Gypsum, KCl i $CaCl_2$, produced from untreated brines, should be treated as waste with enhanced radioactivity. The use or disposal of such waste may lead to the radiation hazard for the population, sometimes annual dose limit (1 mSv) can be exceeded. Therefore disposal of huge amounts of waste materials, for instance 10 tones/hour of $CaCl_2$, may be complicated.

If pretreatment of brines is applied, i.e. purifiaction of radium, no radiation hazard can be observed for the local population and consumers of the desalination products. Nonetheless, monitoring of radium content in these products would be necessary.

A bit different is a problem of scales in the primary system. Even during desalination of previously purified brines, a sedimentation of deposits with radium concentration above 10 kBq/kg would be possible. Of course, the sedimentation advance will be different, and the increase of gamma dose rate and radiation hazard for the crew will be much slower. Only possible danger of the contamination is due to the reparation of elements of installation and uncontrolled release of scales into environment.

The assessment of the CDP impact on the enviroment shows, that no possible hazard for the local population and very low probability of the contamination of the natural enviroment is predicted during desalination of mine waters, previously purified of radium.

Described analysis points out that desalination of mine water has a multidimentional context, not only environmental issue. The problem of impact of brines from Upper Silesian mines must be solved sooner or later. Due to economic reasons, desalination seems to be very expensive and not proper choice. But radium removal from brines must be applied if this technology will be used in the future.

5. Conclusions

I. The problem of negative impact of salty waters, discharge from coal mines, is difficult to solve. One of the possibilities of utilization of brines is desalination. Important issue for desalination technique is radium behaviour during process and resulting concentrations in different products. Such investigations have been carried out in Dębieńsko Desalination plant in 80's and 90's. Due to the fact, that radium concentration (^{226}Ra) in raw brines was relatively low, up to 1.5 kBq/m^3 only, in most products of desalination radium content was also slightly enhanced.

II. Feasibility study of the central desalination plant (CDP) for 3 mines with huge inflows of saline waters has been prepared. Results of the investigations from Dębieńsko are useful to predict radium content in products of designed installation. Taking into account, that average radium concentration in brines from those 3 mines is 3-5 time higher as in Dębieńsko, the assessment has been prepared in 2 variants – without and with radium removal prior to desalination. If brines will be purified in mines, it should be possible to use all products of the desalination process without any restrictions. In other case, possibility of application of some products like gypsum or KCl, could be limited.

III. Desalination of radium-bearing brines will lead to the significant increase of radiation hazards for the crew of the desalination plant. But on the other hand, no significant increase of the environment contamination or hazard for local community is predicted.

IV. The implementation of purification method in Piast Colliery is a significant measure to mitigate radium contamination of the natural environment. A new purification system is under the construction in another mine (Ziemowit). Therefore the desalination of brines from these mines will be possible due to previously done treatment of waters in underground galleries.

References

1. Tomza I., Lebecka J.: *Radium-Bearing waters in Coal Mines Occurrence, Methods of Measurements and Radiation Hazard*, Int.Conf. on Radiation Hazards in Mining, Golden /Co/1981/.
2. J. Lebecka i wsp. - *Monitoring of Radiation Exposure from Different Natural Sources in Polish Coal Mines* - Int. Conference on Occupational Safety in Mining, Vol.2 p.408, Toronto 1985.
3. UNSCEAR 1982 - *Report on Effects of Ionising Radiation*, United Nations, New York.
4. B. Khademi i wsp. - *Transfer of Radium from Soil to Plants in an Area of High Natural Radioactivity in Ramsar, Iran* - Third Int. Conference Natural Radiation Environment.
5. B. L. Dickson i wsp. - *Evaluation of the Radioactive Anomalies Using Radium Isotopes in Groundwaters* - J. of Geochemical Exploration, Vol. 19, p. 195.
6. L. K. Gucało - Geochemia, vol. 12, p. 1305, 1964.
7. I. Gans - *Radium in Waste Waters from Coal Mines and Other Sources in FRG* - Second Symposium on Natural Radiation Environment, Bombay 1981.

8. J. Lebecka i wsp. - *Influence of Mining Activity on Distibution of Radium in Natural Environment* - Int. Conference Isotopes in Nature, p.423, Leipzig 1986.

9. J. Lebecka i wsp. - *Skażenia promieniotwórcze na Górnym Śląsku powodowane przez wody kopalniane i wytrącające się z nich osady* - Wiadomości Górnicze, 6/91, Katowice 1991.

10. *Wytyczne klasyfikacji wyrobisk górniczych oraz bezpiecznego prowadzenia robót w warunkach zagrożenia radiacyjnego powodowanego naturalnymi substancjami promieniotwórczymi* - Wspólnota Węgla Kamiennego, Katowice 1988.

11. J. Lebecka i wsp. - *Wyniki badań zachowania się radu podczas transportu słonych wód rurociągami (na przykładzie kolektora wód słonych OLZA*) - Wiadomości Górnicze 5/92, Katowice 1992.

12. Zarządzenie Prezesa PAA z dnia 19 maja 1989 w sprawie zasad zaliczania odpadów do odpadów promieniotwórczych ż Monitor Polski nr 18 poz. 125, Warszawa 1989.

13. P. M. Huck, W. B. Anderson - *Removal of Ra-226 from Uranium Mining Effluents and Leaching From Sludges* - IAEA, Technical Reports Series No. 310, Vienna 1990.

14. J. Lebecka, B. Łukasik, S. Chałupnik - *Purification of Saline Waters of Radium* - 5th Int. Mine Water Congress, Nottingham 1994.

15. K. Skubacz i wsp. - *Ocena wpływu zbiornika BOJSZOWY na środowisko naturalne* - dokumentacja GIG, Katowice 1991.

16. J. Lebecka i wsp. - Metoda i technologia oczyszczania z radu wód typu B, wyniki badań laboratoryjnych i prób modelowych - Główny Instytut Górnictwa, Katowice, 1994.

17. J. Lebecka i wsp. - Metoda oczyszczania wód typu B z radu - podsumowanie wyników badań prowadzonych dla KWK Czeczott - Główny Instytut Górnictwa, Katowice, 1996.

18. S. Chałupnik i wsp. - METODA I TECHNOLOGIA OCZYSZCZANIA WÓD RADOWYCH TYPU B *KONCEPCJA OCZYSZCZANIA WÓD DOŁOWYCH KWK*

PIAST WRAZ Z WYNIKAMI BADAŃ - dokumentacja grantu KBN, GIG, Katowice, 1997.

19. Urząd Patentowy RP - Patent nr 169869 na „Sposób oczyszczania wód z radu”, dla zespołu pod kierownictwem dr Jolanty Lebeckiej.

20. J. Lebecka, S. Chałupnik, I. Tomza - Badanie zachowania się radu w procesach utylizacji wód kopalnianych - Główny Instytut Górnictwa, Katowice 1988.

21. J. Lebecka, S. Chałupnik, J. Skowronek - Wyniki badania zachowania się radu w procesach utylizacji wód kopalnianych - Główny Instytut Górnictwa, Katowice, 1989.

22. Instrukcja Instytutu Techniki Budowlanej nr 234, ITB Warszawa 1996.

INVESTIGATION OF ABANDONED SURFACE SETTLING PONDS

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INTRODUCTION

One of the problems, which may appear during ground reclamation of surface settling ponds of underground mines, is enhanced radon exhalation from bottom sediments. This problem would become more important, when concentration of radium isotopes in sediments is enhanced due to discharge of radium-bearing waters into pond.

Measurements of radon exhalation have been applied for investigations of different surface settling ponds. One of them was abandoned and emptied at the beginning of year 2002. An agreement of the mine's management and the local authority is to make the ground reclamation of the pond. Because of elevated radium concentrations in thick layer of sediments measurements of different elements of radiological hazard were made such as radon exhalation coefficient, variations of gamma radiation background and radium content in bottom sediments. Additionally radium transfer to vegetation that had transgressed into the pond has been calculated.

The obtained results showed that mentioned above sources of radiation hazard must be taken into account for planning and designing of reclamation operations for surface settling ponds of underground mines.

2. APPLIED INVESTIGATION METHODS AND CHARACTERIZATION OF THE TEST SITES

The principal factor as measured to identify the state of radiological contamination in the abandoned settling ponds areas is the radon exhalation coefficient.

Radon exhalation coefficient is the quantity, which defines its ability to escape from the intergranular porosity of rocks and soils and to transfer into the atmospheric air. Calculating the radon exhalation coefficient requires laboratory determination of various soil parameters. The field measurements allow avoiding the time-consuming and complicated laboratory measurements and provide a good basis of radon potential of the study area.

The measurements have been made using the field method of measuring the radon exhalation coefficient developed at the Central Mining Institute (Chalupnik, Wysocka, 2003). At the test sites the measurements of the variations of the natural gamma radiation background and the spectrometric analyses of the settling pond bottom sediment samples have been made. In one of the ponds being under study, where the natural plant ingress had taken place, the measurements of radium isotopes content of the plant samples were taken.

3. DISCUSSION OF MEASUREMENT RESULTS

3.1. The measurements in the areas not disturbed by mining operations.

To determine the radon exhalation coefficient range for the area of Upper Silesia the measurements have been made at the sites not influenced by mining activity. It has been found that radon exhalation depends on the geological structure of a subsurface layer. The majority of the measured values have ranged from 2 to 50 mBqm^{-2}s^{-1}, which are being considered as the average ones in normal conditions (Myrick, at al., 1983). The highest values were obtained from the outcrops of Triassic carbonate rocks. At those sites the radon exhalation exhibited the widest range of values of from 1 mBqm^{-2}s^{-1} to 80 mBqm^{-2}s^{-1} (Chalupnik, Wysocka, 2003). The values of radon exhalation coefficient over the outcrop areas of different lithostratigraphic units are summarised in Table 1 (Wysocka 2002).

Tab.1. The values of radon exhalation coefficient and radon in soil concentrations at outcrops of different geological formations.

Site of measurements/ Startigraphy	Radium ^{226}Ra concentration in sediments *Range* [Bq/kg]	Radon ^{222}Rn in soil-gas *Range* [Bq/m^3]	Radon ^{222}Rn exhalation coefficient *Range* [mBqm^{-2}s^{-1}]	Radon ^{222}Rn exhalation coefficient *Arith. mean* [mBqm^{-2}s^{-1}]
Triassic rock outcrops	11-51	120 - 66750	1.6 – 80	15.0
Carboniferous rock outcrops	11-65	15370 - 27870	6.4 – 27.0	16.0
Miocene	11-43	170-7500	1.6-2.5	2.0
Quaternary	15-29	120 - 58000	1.6 – 7.0	3.5

3.2. The measurements in surface settling ponds

The measurements were made in three surface settling ponds being under closure operation. Before then the mine underground waters of different chemical composition and different natural radionuclide concentration had been discharged into the mentioned above ponds.

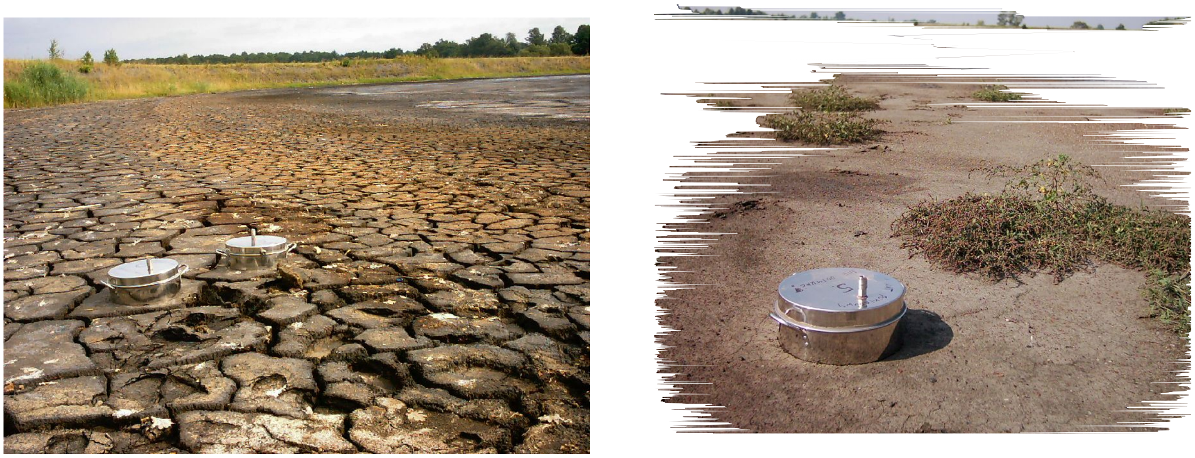
Settling pond A

The measurements in the settling pond A were being taken during its filling with waste rock. The spectrometric analysis of the pond's bottom sediments has shown that the maximum radium ^{226}Ra concentration was around 3.0 kBq/kg. The measurements of radon exhalation coefficient were taken both in the part of the pond where the bottom sediments were just covered by a waste rock layer of more then 10 m thick and in the part of pond where the dried bottom sediments had not before been covered by any isolating layer. The radon exhalation coefficient measured over the dried bottom sediment amounted to about 12 $mBqm^{-2}s^{-1}$. This value appears to be within the range of average values (Wilkening, 1972) and within the range of values obtained from the measurements taken at outcrops of Carboniferous rocks over Upper Silesia (Wysocka, 2002). The radon exhalation coefficient in the covered part of the pond were low and did not exceed a value of 2 $mBqm^{-2}s^{-1}$, as compared with the value of 3.4 $mBqm^{-2}s^{-1}$obtained from measurements at the nearby old waste rock dumping ground. The insignificant increase of the exhalation for the waste rock from the heap as compared with the corresponding factor for the piled up broken waste rock material freshly drawn out from the mine can be regarded as being due to the increased sealing of the heap which reduces the radon gas seepage towards the atmospheric air. It is to be expected that drying and afterwards covering of the pond's bottom sediments by waste rocks from the adjoining heap can be a satisfactory protection measure against the radon gas emission

In the vicinity of the pond the disturbances of the natural gamma radiation background has been measured. On the basis of the measured values of kerma the ambient dose equivalent rate were calculated. The gamma dose rates ranged from 0.1 to 0.2 μSv/h and appeared to be higher than the corresponding average values for the area of Upper Silesia (see Fig. 3).

Settling pond B

The waters with enhanced natural radioactivity from two hard coal mines, had previously been discharged into the settling pond B. In this case, the problem of possible radiological hazard caused by the enhanced exhalation of radon appeared to be more serious then in the case of pond A. That is because the settling pond area is about 16 hectares and the thickness of accumulated sediments amounts to 1m. The total radium radioactivity in discharged waters was up to 120 MBq per day. Taking the statements mentioned above into the consideration, the measurements were regularly made in the settling pond area during the spring – autumn period in 2002 and 2003. The results of the spectrometric analysis have shown that in the bottom sediments maximum radium ^{226}Ra and ^{228}Ra concentrations amounted to 2.0 kBq/kg and 4.0 kBq/kg respectively. In spite of nearly one year drying of the sediments, the high ground water level made it impossible to measure the radon in soil concentration. In the case of wet soils the measurements of radon exhalation coefficient proves to be useful tool that allows assessing the occurrence of the increased radon emission.



a. the first year of measurements, b. the second year of pond B measurements

Fig. 1. The measurements of radon exhalation coefficient at the bottom of an abandoned surface mine water settling pond.

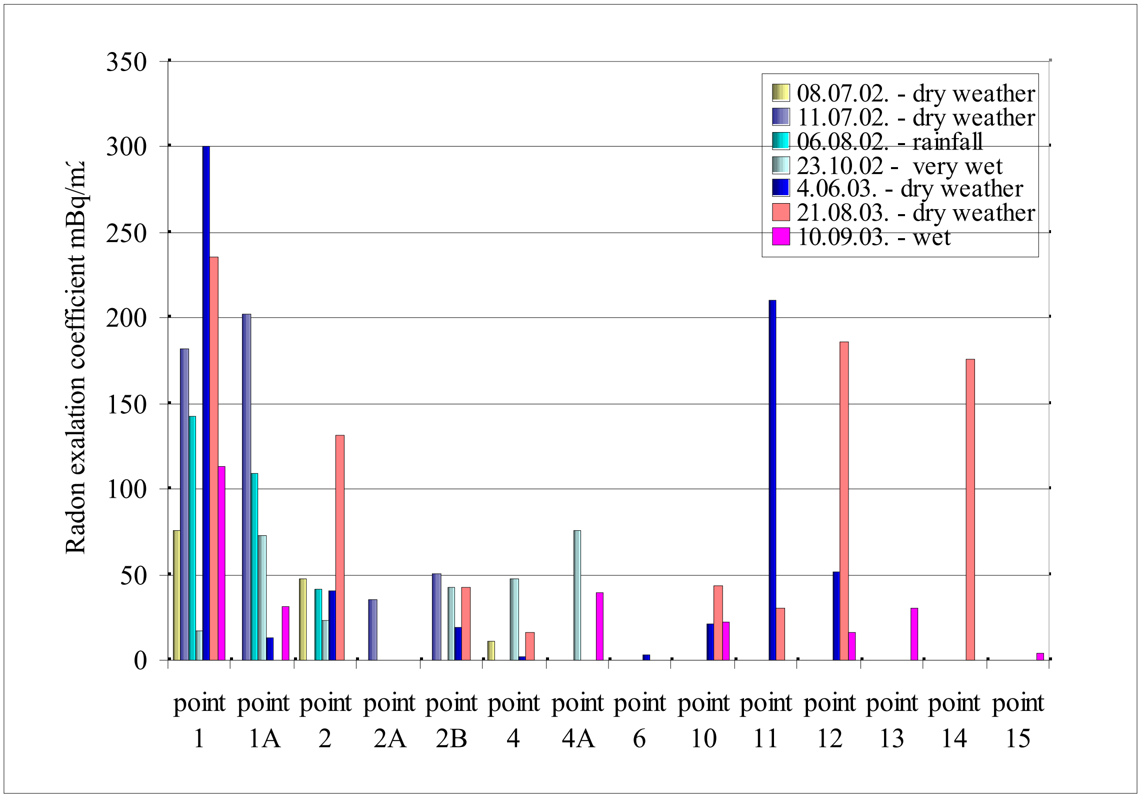


Fig. 2. Results of radon exhalation coefficient measurements performed in settling

The measurements of the radon exhalation were made under different weather conditions in the years 2002 –2003. The first measurements were taken in July following a period of several weeks of rainless weather. Certain parts of the pond were so dried that it was possible to enter them and install diffusion chambers (Fig.1a). The obtained values of the radon exhalation coefficient ranged from around 2 mBqm^{-2}s^{-1}to more than 70 mBqm^{-2}s^{-1} . The subsequent measurements made after a week of sunny, rainless weather showed a significant increase of radon exhalation up to more than 160 mBqm^{-2}s^{-1}. The measurements were repeated approximately every two weeks up to the last days of October 2002. The dried area of the pond's bottom grew larger allowing us to increase the number of recording sites. The highest value of radon exhalation coefficient obtained in the first year of investigations was 202 mBqm^{-2}s^{-1} being considerably recorded through the area of Upper Silesia (Chalupnik, Wysocka). It is important to note that whole the first year of investigations sediments of settling pond B were wet and the radon emission only took place from their thin subsurface layer, the thickness of which ranged approximately from 0.1 to 0.2 m.

In the second year of measurement, the settling pond's bottom was being dried enough to allow us to perform investigation throughout most of the pond's area. The water level was much lowered and the radon gas emanation was expected to come from a layer considerably thicker than that in the previous year. The results from measurements made in June following a longer rainless period, indicated that radon gas emission measured at the most intensely dried sites of the settling pond exceeded the previous year's emission.

At recording point No.1 the radon exhalation coefficient was around 300 $mBqm^{-2}s^{-1}$. At the sites where no measurements had been made before high values were obtained as for instance those of more than 200 $mBqm^{-2}s^{-1}$ at point 12 and about 50 $mBqm^{-2}s^{-1}$ at point 13 (Fig.2). The succeeding measurements showed that high radon emission persisted even after rainfall periods – about 100 $mBqm^{-2}s^{-1}$. During the rainy periods the wet subsurface layer notwithstanding the high radon gas emission persisted, exceeding the values recorded over the Upper Silesia Coal Basin area. The values of the radon exhalation coefficient measured in the vicinity of the settling pond did not exceeded 3 $mBqm^{-2}s^{-1}$. Such as intense radon exhalation as that measured over the abandoned settling pond B area has not been found at any other test site.

In order to obtain more information on radiation hazards, the measurements of the variations of natural gamma radiation background were made over the pond B. On the basis on measurements of kerma, the values of ambient dose equivalent rate were calculated. The results of the measurements are shown in Fig. 3. The calculated values many times exceeded the average value for either Upper Silesia or the whole area of Poland (Radiological Atlas, 1998) and ranged from 0.6 to 2.6 μSv/h.

In order to investigate the influence of the settling pond B on the ecosystem the samples of the vegetation that began to overgrow the dried bottom sediments were collected. The vegetation transgression commenced in spring 2003, starting from the dried places where the salt water from the subsurface layer was either washed out or diluted by precipitation (Fig.1b.). Samples of pigweed and reed growing on the bottom sediments at some distance of the pond bank were collected. The radium ^{226}Ra and ^{228}Ra isotope content of the plants were determined and compared with data from publications (Table 2). Although each cited group of results refers to a different kind of vegetation, it however gives a general picture of the naturally encountered concentration ranges. According to our archive data the radium concentrations in grass samples collected in the vicinity of settling pond B do not exceed 5 Bq/kg. However current investigations of plant samples collected from the bottom sediments show the radium concentrations reaching the values of 138 Bq/kg and 237 Bq/kg for radium ^{226}Ra and ^{228}Ra (dry mass) respectively. By far higher radium concentrations were obtained from measurements taken on grass samples collected in the areas contaminated with sediments of higher radioactivity near place Rybnik-Boguszowice in 1980s (Lebecka et al., 1986). The average radium content was 142 Bq/kg with the maximum value in excess of 900 Bq/kg. The radium transfer from soil to plants was the area of research conducted by Ms.L.Rosiak (Rosiak, 2003). According to the results of her study, the radium ^{226}Ra concentrations in various plants raised in the experimental plots did not exceed 3 Bq/kg. The radium ^{226}Ra concentrations in the used for the experiment soil were much lower than in the Bojszowy settling pond and did not exceed 12 Bq/kg.

The total radium transfer factors TF1 calculated for the settling pond B plant growth are contained within the ranges given by L.Rosiak (Table 2). Thus the preliminary results from the analyses of the impact of post mine wastes on plant radiological contamination point to attaching importance to the problem, which the mines and local communities will have to cope with in the future. According the researches dealing with the problem of the radium transfer from soil to plants, radium ^{226}Ra content of plants under normal conditions, ranges from 0.001 Bq/kg to 11 Bq/kg

(Simon and Ibrahim, 1990). In the light of the reported data, the measured radium content of the plants growing at the abandoned settling pond bottom is many times in excess of the radium content regarded as being the average one encountered in the natural environment.

Table 2. Comparison of radium isotope content of plant samples collected from the settling pond B and the corresponding data presented in the publications.

Sampling site	Radium content ^{226}Ra Bq/kg (dry mass)	Radium content ^{228}Ra Bq/kg (dry mass)	Radium transfer factor TF1 ^{226}Ra	Radium transfer factor TF1 ^{228}Ra
Settling pond B, about 1 m off the bank, near the water inlet No. 1.	138 ± 11	237 ± 47	$6.9 \cdot 10^{-2}$	$5.9 \cdot 10^{-2}$
Settling pond B, about 2 m off the bank, near the water inlet No. 2.	66.3 ± 5,3	84 ± 16	$3.3 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$
Neighbourhood of settling pond B.	1.7 ± 0.2 – 4.8 ± 1,4 (avg. 3.3)	1.3 ± 1 – 4.8 ± 1.4 (avg.2.2)	-	-
Rybnik-Boguszowice	6±4 - 973±97 (avg. 325)	3±2 – 168±33 (avg. 49)	-	-
According to L. Rosiak 2003	0.03±0.01–2,96±0,11 avg.. 0.75	no data	$0.54 \cdot 10^{-2}$ do $51 \cdot 10^{-2}$	no data
According to Simon, Ibrahim, 1990	0,001 – 11	no data	-	-

Settling pond C

To compare situations arising at various settling ponds abandonment stages the measurements were made in settling pond C. The pond was evacuated in 1980s and the sediments were moved to an old sand pit and than the water was again being discharged into the repaired settling pond. The sediments from the pond's dredging operation showing radium ^{226}Ra concentration values in excess of 100 kBq/kg were covered with the waste rock forming, in course of time, a heap of refuse about 20 m height. The measurements of radon exhalation were taken on both the waste rock pile covering the sediments and the active settling pond bank. On the settling pond bank radon exhalation coefficient reached values of about 20 mBqm^{-2}s^{-1} while on the waste rock pile the corresponding values did not exceed 2 mBqm^{-2}s^{-1}. In the vicinity of the settling pond natural gamma radiation background perturbation measurements were made as well. Just as in the case of radon exhalation, the ambient dose equivalent rates were higher for the pond bank and lower for the waste rock pile. The obtained values (Fig. 3) are lower than those typical for settling pond B, but they still can many times exceed the average values for Upper Silesia. The waste rock covered sediments, at present, pose no radiation hazard for the natural environment. However it is important to note that if these sediments are exposed, as a result for instance of the waste rock pile stripping to recover rock material for use in highway engineering, the radon emission will be intensified, the natural gamma radiation background will be perturbed and the radium will even transfer to plants.

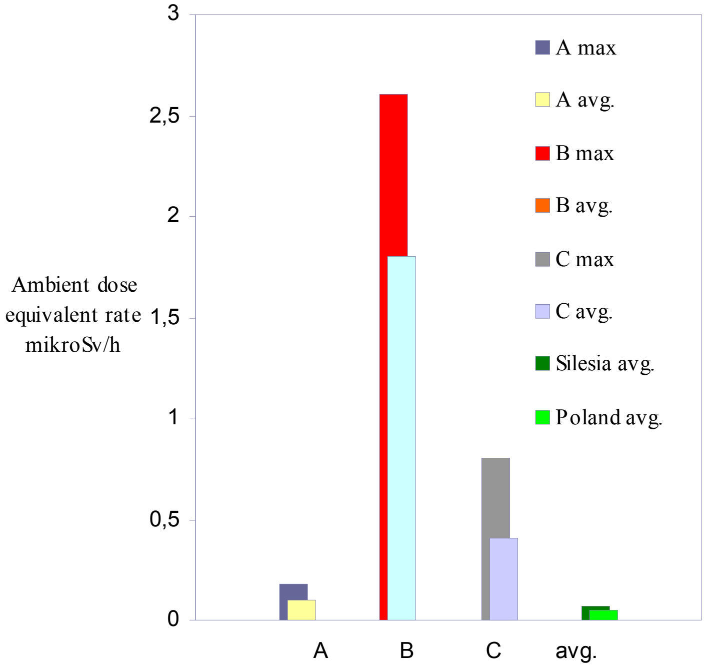


Fig. 3. The results of measurements of the variations of the natural gamma-radioactivity background in the areas of abandoned settling ponds.

SUMMARY

The comparison of the results from the measurements of radon exhalation and of radium content of the mine water settling pond bottom sediments is shown in Fig. 4. The highest values of radon exhalation coefficient have been obtained from the measurements taken at the bottom of settling pond B. In the two remaining settling ponds the measurements showed low levels of radon exhalation coefficient. No correlation was found between the radon exhalation and its parent isotope – radium content of bottom sediments. In settling pond B which showed the highest value of radon emission, the radium concentration in bottom sediments is comparable to that measured in settling pond A, where the lowest value of radon emission was found. In the contrary, in the area of accumulation of sediments of high radium content (wastes from settling pond C), low values of radon emission were measured.

The described above examples of different mine water settling ponds show that in each case there is a different scheme of radon escaping to the atmosphere. The mere findings of high radium concentrations in bottom sediments do not give ground for assuming that the radon exhalation from these places can be high as well. And on the contrary, in places where natural radioactivity of bottom sediments is being far from extreme ones, radon emission may be intensified. Settling pond B can be an example of such a place. The radon ability to migration from ground and soil intergranular porosity depends however on many factors composing its physical characteristics. Therefore radon exhalation coefficient can reach very high values even if the values of radium concentrations in the bottom sediments being investigated exhibit relatively low values.

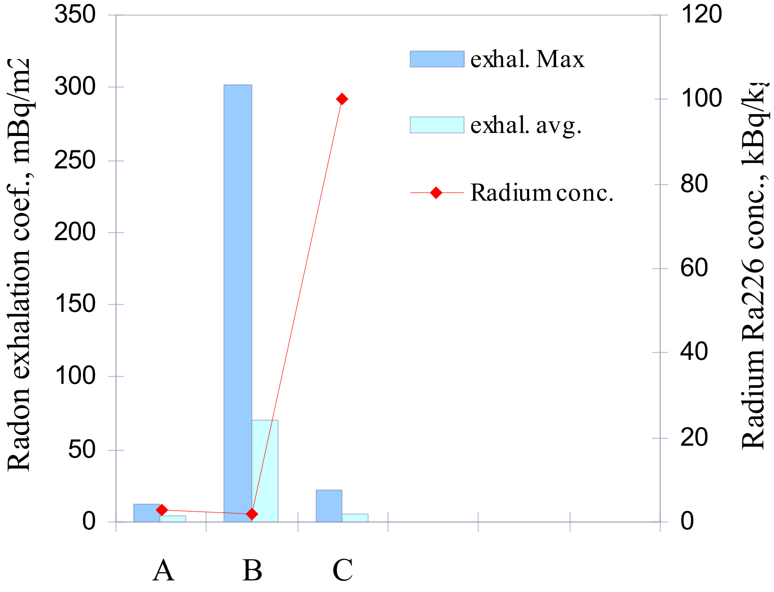


Fig. 4. Comparison of radon exhalation coefficient and radium content of bottom sediments from the abandoned mine water settling ponds.

CONCLUSIONS

The measurements carried out within the abandoned mine water settling ponds show that measures undertaken in connection with mine closure operations may have a severe impact on the surrounding environment evidenced, among others, by following phenomena:

- intensified radon emission poising potential radiation hazard for the residents and tenants of buildings founded in the reclaimed settling pond areas;
- variations of the natural gamma radiation background
- radiological plant contamination resulting from radium transfer from the sediments with elevated radium content.

In the described cases the radiation hazards induced by high radon exhalation, elevated gamma radiation rates and high radium content in sediments can be confident to not large areas, situated at considerable distances from buildings. It is generally known that in Polish mines the systematic measurements of all the radiological hazards – related elements, have been carried out since 1986. Therefore a possibility of the radiological contamination “spots” formations resulting from the past uncontrolled surface disposal of bottom sediments from mine workings, as for example the sediments from pumping stations and water galleries, cannot be ruled out. Possibly detailed future measurements carried out within both the active and closed mines areas, would show radiation hazard areas comparable to that described above.

The assessment of radon emission level from the bottom sediments is the essential information pointing to the way the post settling pond areas can be reclaimed. In the case of increased radon exhalation the sediments sealing should be planned so as to avoid migration and penetration of that gas into the future buildings that might be built in the areas of settling ponds.

REFERENCES

1. Chałupnik S., Wysocka M., Pomiary ekshalacji radonu z gruntu – opracowanie metodyki i pomiary wstępne, (Measurements of radon exhalation from ground – development of the method and preliminary results) Prace Naukowe GIG, Katowice, 1/200, 2003.
2. Lebecka J. I wsp., Wstępna ocena stopnia skażenia radem wytrąconym z wód kopalnianych na terenie miejscowości Rybnik-Boguszowice, (Preliminary assessment of the level of contamination caused by radium precipitated from mine water in the area of Rybnik-Boguszowice), Dokumentacja wewnętrzna GIG, 1986.
3. Myrick T.E., Berven B.A., Haywood A.A., 1983, Determination of concentration of selected radionuclides in surface soil in U.S., Health Phys., 45, 631.
4. Radiologiczny Atlas Polski, (Radiological Atlas of Poland), 1998, PIOŚ, CLOR, PAA, Biblioteka Monitoringu Środowiska, Warszawa.

5. Rosiak L., Badanie przechodzenia ^{226}Ra z gleby do roślin oraz ocena wchłonięć tego radionuklidu z pożywieniem, praca doktorska, (Investigation of radium ^{226}Ra transfer from soil to plants and assessment of intakes of this radionuclide with food, Doctor's thesis), Główny Instytut Górnictwa, Katowice, 2003.
6. Simon S.I., Ibrahim S.A., Biological uptake of radium by terrestrial plants. Technical Reports Series No 310, The environmental behaviour of radium, Vol. 1, IAEA, Vienna, 545-599, 1990.
7. Wysocka M., Zależność stężeń radonu od warunków geologiczno-górniczych na terenie Górnośląskiego Zagłębia Węglowego, (Dependence of radon concentrations on the area of Upper Silesian Coal Basin on geological and mining conditions), Prace Naukowe GIG, Katowice, 3/2002, 2002.
8. Wysocka M., Chałupnik S., Correlation of radon concentration level with mining and geological conditions in Upper Silesia Region, Journal of Mining Science, Vol. 39, No.2. 2003.

NORM LEGISLATION IN POLAND

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Abstract

Polish Parliament (Seym) established November 29, 2000 new Atomic law, changing it significantly many regulations in compliance with EU law. Atomic Law is in force since January 1, 2002.

In this act the regulations of peaceful appliance of the atomic energy, real and potential risk due to the ionizing radiation from the artificial sources of radiation or nuclear materials, nuclear wastes and used nuclear fuel. The regulations of the nuclear safety, radioprotection of human and environment has been described in this act, too.

In July 2001, Seym changed significantly Polish Geological and mining law. This act is valid since January 1, 2002. In this act the regulations for the radioprotection of workers from natural sources of ionizing radiation were significantly modified.

In this paper these new regulations are described with a special emphasis on the lack of detailed regulations as regards of the mining wastes with enhanced natural radioactivity.

Introduction

In the common perception the danger of the ionizing radiation is connected mostly with the use of the atomic energy for military, power industry or medical purposes. Even today not everyone realizes that a human being has always and everywhere been disposed on ionizing radiation, and the share of natural sources of such radiation reaches ¾ of a dose an average Pole receives.

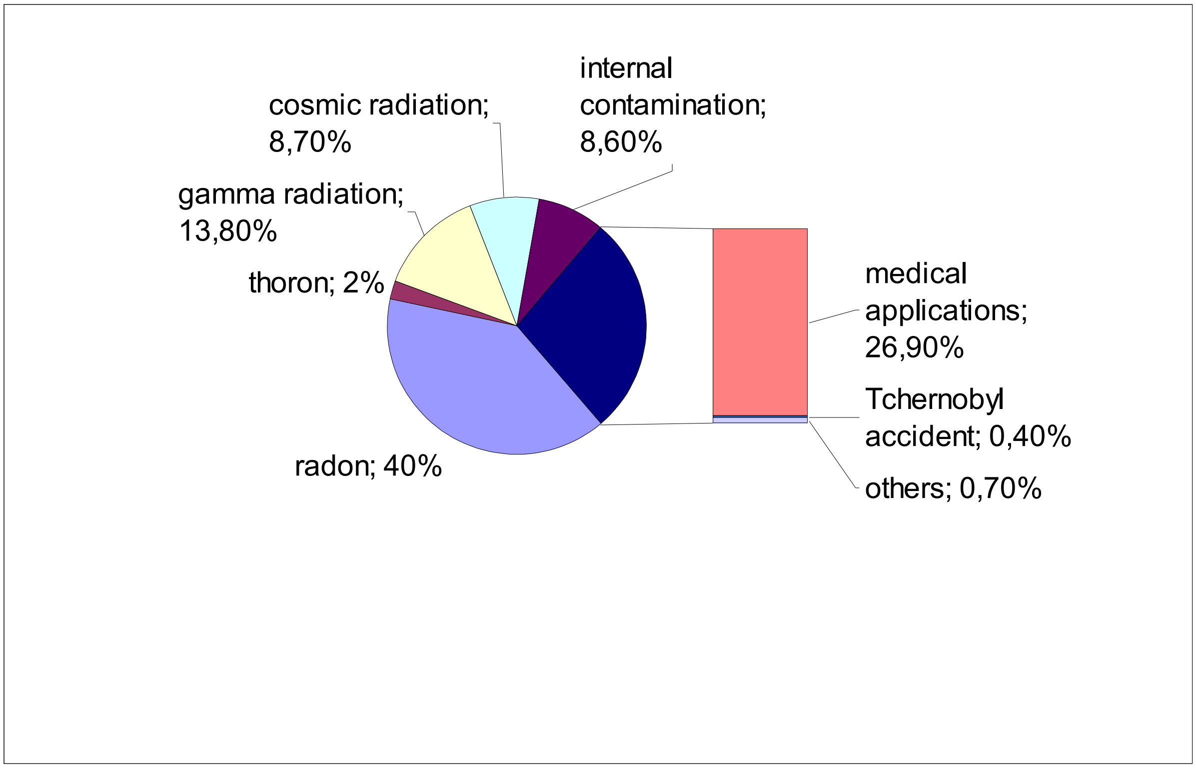

Fig. 1. The components of a dose of the ionizing radiation (3,3 mSv per year) a typical Pole receives

In many cases, from uranium or thorium ores and other mining branches to treatment of mineral substances, doses are augmented as the result of technological processing.

Until the year 2000 the Polish *Nuclear Law* did not mention the natural radiation and the hazard it may bring. The whole attention was devoted to “the use of atomic energy for the social and economic needs of the country” and problems connected with endangering employees and incidental persons to ionizing radiation. In other words – it dealt with artificial radionuclides and the use of ionizing radiation from nuclear devices and systems.

Legal regulations in other countries were similar, actually. Only in the 90’s world organizations of radiological protection added to their recommendations the question of the protection against ionizing radiation form natural sources changed by the industrial activity.

Several mnemonic abbreviations are used to describe materials of higher concentration of natural radioactive isotopes. We can found:

NORM - normally occurring radioactive materials,

TENR - technologically enhanced natural radioactivity,

TENORM - technologically enhanced normally occurring radioactive materials.

The following definition can be adopted:

TENORM – *a natural substance, raw material or other material that is not a subject of legal regulations binding for the use of the atomic energy or artificial sources of radiation, that was mined, processed or present in other processes connected to any activity that may cause a relative increase of exposing for the ionizing radiation and the radiation risk involved for the employed or other people present in its neighbourhood, over the natural background.*

Radioprotection in the law of the European Union

The importance of questions of the radiological danger from natural radioactive isotopes is confirmed by the Directive of 13 May 1996 of the Council of the United Europe, titled *The EC basic safety standards for the protection of the health of the workers and the general public against dangers arising from ionizing radiation*, what introduced specific regulations in this area. Although such dangers were covered by special rules before, they were not directly included in EU regulations. However, it was emphasised that the requirements of the mentioned act do not apply to risks arising from the radon in habitable buildings, dangers connected to radionuclides being a part of a human body or the cosmic radiation on the Earth's surface and from the hazard over the surface from radionuclides of the unbroken lithosphere.

In the chapter VII, the Directive places the member countries under the obligation to identify areas of professional activities where the danger arising from ionizing radiation of natural radioactive isotopes may occur on the important level as regards the radiological protection. Such requirement applies particularly to:

- professional activity during which workers and/or incidental persons are endangered by the alpha radiation from radon isotopes and its daughters and the gamma radiation. Every underground mine and cave is given as an example here;
- professional activity connected to exploitation, processing and storing substances normally not considered as radioactive, but containing natural radioactive nuclides causing a significant growth of hazard for workers and incidental persons (where applicable);
- professional activity that results in formation of waste normally not considered as radioactive, but containing natural radioactive nuclides and causing a radiation hazard for incidental persons and workers (where applicable);
- air traffic.

If a member country recognizes a professional activity as radiologically endangering or there is a probability of occurring such danger, the Directive places such country under an obligation to monitor appropriately the hazard and if needed:

- to start actions to decrease the radiation danger
- to use means of radiological protection similar to those for hazard arising from artificial radioactive isotopes, resulting from the mentioned Directive.

The direct responsibility of the realization of requirements of the radiological protection is delegated, on the basis of Article 47, on an employer or producer of wastes containing TENORM substances.

Because of the fact that the requirements set by the Directive are not precise as regards the definition of areas where the hazard of TENORM substances may occur, recommendations were provided by experts and issued by one of Directorates-General of the European Commission in order to facilitate the incorporation of regulations of the Directive 96/29 to the internal legal regulations of the member countries. Criteria of assessment and selection of endangered areas, the optimization of prevention measures and requirements for monitoring are given there. Also, the examples of the NORM phenomenon are given, important as regards the radiological protection. Here are:

- production of the electric energy on the basis of mineral fuels,
- phosphorites processing and the use of phosphates
- petroleum and gas production
- zinc and lanthanides production
- metallurgy of the iron and non-ferrous metals
- ores output and copper production

Generally, the discussed directive gives the member countries the wide possibility of interpretation of the radiation danger caused by NORM phenomenon. The basis for such actions is a compromise in the estimation of such risk, where the primary criterion is the effectiveness and measurable results. The levels of actions depend on financial resources of a country.

The EU member countries were obliged to readjust their internal regulations to the requirements set by the directive up to 13 May 2000.

Radioprotection in the Polish law

On 29 November 2000 the Polish Seym amended the *Nuclear Law* by changing the most of its requirements and readjusting them to the European law. The amended act came into force on 1 January 2002.

The Act describes the rules of the peaceful use of the atomic energy connected to the real and potential risk of the ionizing radiation from artificial sources, nuclear materials, devices producing the ionizing radiation, radioactive waste and burnt nuclear fuel. These actions are acceptable when requirements of the nuclear safety, radiological protection of people, environment and property protection are met and after obtaining an appropriate permission.

According to article 1 point 3 of the amended act:

the act shall be applied also to actions performed in conditions of ***the increased hazard of the ionizing radiation resulted from the human activity.***

Also, the act describes duties of a chief manager of an organizational unit performing such activity, authorities adequate in nuclear safety issues and radiological protection and rules of the civil responsibility for nuclear damages. These damages may also include negative results of the increased hazard of natural sources of ionizing radiation.

In article 13 item 1 of the act it is underlined that:

dose limits do not cover the hazard of the natural radiation if this hazard <u>has not been</u> increased as a result of the human activity, *especially they do not include the hazard of the radon in dwelling houses, of natural radiating nuclides being a part of a human body, of the cosmic radiation at the Earth's surface and of underground hazard of nuclides in the unbroken lithosphere.*

It is considered as controversial to exclude the danger caused by the radon in dwelling houses, because in many cases its concentration may be high enough to cause that the dose for inhabitants is close (or even higher) to the limit; that concentration depends also on human activity (type of building materials, type of constriction or type of use of a building). This problem will be discussed in the second part of the present paper.

Article 23 of the amended act demands to assess the danger from natural radiating isotopes in underground mines, also. The assessment is made on the basis of dosimetric measures in the work environment. A manager of an organizational unit is responsible for such assessment and all actions to lower the danger.

Another important requirement, present in the Polish *Nuclear Law* for the first time, is that the monitoring of individual doses and internal contaminations shall be performed by laboratories with accredited methods of measurement. Results of the individual monitoring are stored in the central register of doses kept by the President of the National Atomic Energy Agency.

The President of the National Atomic Energy Agency, on the basis of the mentioned act, is obliged to assess systematically the situation of the country as regards the radiation. He/she is allowed to demand from every institution, organization and person to make all collected information available (art. 79).

Administrative regulations to the *Nuclear Law* Act

The decree of the Council of Ministers of 28 May 2002 *on dose limits of the ionizing radiation* is fundamental for the radiological protection. The decree sets the value of a dose limit, presented as a effective dose, on the level of 20 mSv yearly. It allows to exceed this dose up to the value of 50 mSv yearly on condition that during the five consecutive years the sum of doses will not exceed 100 mSv. Pregnant women cannot be employed in conditions that may cause the baby to receive a dose over 1 mSv/year, and breast-feeding mothers cannot be employed in conditions that may cause internal or external contaminations. For trainees and students of 16-18 years of age the dose limit is 6 mSv/year, and for the younger and all population – 1 mSv/year. There is no difference whether the dose is caused by the radiation from artificial sources or devices emitting ionizing radiation, or the increased exposure to the ionizing radiation from natural sources, resulted from the human activity.

The requirement to take into account the value of the radiation background when estimating the doses of the ionizing radiation is a novelty. The considered value of the background should be on the level typical for the given area (if it is not known – the average value for Poland: 2,4 mSv per year); also, the actual time of exposure should be considered. In other words – the value of the dose of the background received in the given period of time should be subtracted form the measured value of the dose.

Formulas to evaluate doses and danger ratios tables are presented in annexes to the decree.

Requirements for work with sources of the ionizing radiation are given in several other decrees concerning, among other things, documents required when submitting application for permission for activity connected to the exposure to the ionizing radiation, conditions of safe work with sources of the ionizing radiation, radioactive waste, monitored and checked areas, procedure of granting the rights of a inspector of the radiological protection, recording of individual doses, dosimetric devices and emergency procedure in case of radiation incidents.

The activity connected to the exposure to the ionizing radiation, described in the article 4 of the *Nuclear Law,* may be performed on condition of obtaining an appropriate permission from the President of the National Atomic Energy Agency. Documents required when applying for the permission[8] have to include, among other things, grounds for taking such activity, information on sources and radioactive waste being formed (appropriate instructions, regulations and emergency procedure included), rights of the employed[12], the range and type of monitoring the exposure of employees, programme of providing the quality of the activity. In cases described in a separate decree, when the expected exposure is not too high, the registration is sufficient. It should be underlined that an employer is obliged not only to monitor the danger but also to register doses received by employees of the A category of risk[13].

Every person of this category will have his/her own card of record in the central register of doses, kept by the President of the National Atomic Energy Agency.

Proceeding with the radioactive waste is regulated by the decree of the Council of Ministers of 3 December 2002 *on the radioactive waste and burnt nuclear fuel*[10]. The limits of content of radioactive substances are described there, exceeding which will result in including the waste to radioactive wastes. Wastes are included to an appropriate category on the basis of the value of activity and radioactive concentration of isotopes given in annex 1 to the decree.

The radioactive wastes are divided in three categories:

- warm – if the radioactive concentration of an isotope does not exceed 10 thousand times the values given in the annex,
- of the average activity – if the radioactive concentration of an isotope exceeds 10 thousand times but does not exceed 10 million times the values given in the annex,
- of the high activity – if the radioactive concentration of an isotope exceeds more than 10 million times the values given in the annex.

Three subcategories of wastes are set for each category, regarding the half-lives of isotopes they contain: transitory, short-lived and long-lived.

Also, the decree creates a separate category for burnt closed radioactive sources, which are then qualified as regards the level of activity to the subcategories: warm, of the average activity and of the high activity.

It is not allowed to dilute radioactive wastes in order to lower the concentration of the isotopes.

The decree numbers the requirements concerning the record and storage of wastes and models of information tables.

According to par. 4 of the decree

masses of soil or rock, removed or displaced because of an investment or exploitation of minerals, together with the processing, containing natural radionuclides, shall not be qualified as warm radioactive waste if the sum of ratios of *maximum radioactive concentrations of these isotopes, resulting from inhomogeneity of wastes, to the values described in the annex 1 to the decree, does not exceed 10 for a representative probe of waste of 1 kg.*

The above refers to the act *on wastes* as regards excluding of masses of soil and rock described this way from regulations of the nuclear law, on condition that the appropriate requirements are met. It allows to avoid a complicated legal procedure set for radioactive wastes, in case of a huge amount of wastes containing increased quantity of natural radionuclides produced both in mining industry and other.

Now, mining sediments that sum of concentrations of the radium isotopes ^{226}Ra and ^{228}Ra is lower than 100 kBq/kg will not be treated as the warm radioactive waste. However, there is still the problem how to deal with masses of rock and wastes that the content of natural radionuclides does not exceed such limit but is much higher than average in nature. It is undeniable that it may cause employees or incidental persons to receive increased doses resulting form their activity.

Radioprotection in the mining law

For the first time problems of protection of miners form natural sources of ionizing radiation were formulated in the Polish Standard *Radiological protection in underground mining plants* at the end of 80's. The sources of hazard from ionizing radiation emitted by natural radioactive substances were defined there. The Standard set the limits of the danger for miners, both the dose limit and labour limits. The requirements for methods and devices to monitor the danger were given. The detailed regulations concerning monitoring and prevention were to be set separately for every branch of the mining industry. For coal mining, instructions for danger monitoring and guidelines for preventing the radiation hazard were developed.

Coming into force of the new *Geological and Mining Law* and its administrative regulations in 1994 made a part of the Standard out-of-date. On the basis of the mentioned act the President of the State Mining Authority issued an ordinance on criteria of estimation of natural dangers and including an excavation to an appropriate class of hazard, and the Minister of Industry and Trade – a decree on the industrial safety. These regulations were binding for all branches of the mining industry.

In July 2001, the Polish Parliament resolved the act on amendments to *Geological and Mining Law* what changed the regulations fundamentally. The amended *Geological and Mining Law* became effective on 1 January 2002. Because of that fact, regulations concerning natural hazards in the mining industry were modified.

The article 73 of the amended act places an entrepreneur under the obligation not only to recognise the danger, to undertake actions to prevent and eliminate it, but also to estimate and evidence the professional risk occurring in a mining plant. The art. 73 item 1, among other dangers in mines, mentions the radiation hazard of natural radioactive substances, also.

The constitutional requirements concerning law sources and regulations set by the act of 4 September 1997 on government administration divisions decided that art. 73a item 3 of the amended act obliged the Prime Minister to establish, in a decree, criteria of estimating natural hazards and the procedure of classifying deposits (ledges), their parts or excavations to an appropriate levels (categories, classes) of danger. The minister for economic matters shall establish detailed regulations regarding the industrial safety, work running and rules of estimating and evidence of the professional risk and the use of necessary preventive measures (art. 78 of the act).

The decree of the Minister of Interior and Administration *on natural dangers in mines* divided underground excavations into two classes of the radiation hazard:

- A class excavations – the environment of work where an employee may be exposed to an effective yearly dose exceeding 6 mSv,
- B class excavations - the environment of work where an employee may be exposed to an effective yearly dose over 1 mSv but not exceeding 6 mSv.

It is needed to remember that the levels of doses presented here already include the influence of the natural background on results of measures and estimation of the danger – according to the requirements of the *Nuclear Law*. In other words, when classifying excavations to categories of the radiation hazard, the value of dose of the background received in the given period of time should be subtracted form the measured value of the dose.

The decree describes the measures of sources of the radiation danger that shall be the basis for classification of excavations. The following ratios of danger from natural radioactive substances are defined there:

- the concentration of the alpha potential energy of the short-lived radon daughters,
- the power of a dose of the gamma radiation,
- the radon concentration in waters,
- the radium specific activity in sediments.

In the Decree of the Minister of Economy *on industrial safety, work running and technical fire protection in underground mines*, there are regulations concerning the protection against natural (section V chapter 7) and artificial sources of the ionizing radiation (section VI chapter 7). The rules regarding the natural sources of the radiation danger are going to be discussed here.

The decree does not use the term of the dose limit provided by the nuclear law. Par. 386 gives the definition of a dose constraint what actually is the same in all mining industry:

In underground mines, in excavations endangered radiologically, what means those where there is a possibility of receiving a yearly effective dose over 1 mSv, introduced methods shall preclude exceeding the usable limit of 20mSv.

Consequently, it is not possible that the danger from natural radioactive substances in a mine in a given year was higher than 20 mSv – what the nuclear law allows.

Measures of the danger of natural radioactive substances are carried out in every underground mine, and in a mine where such danger occurs its level is estimated, also.

Excavations of the B class of the radiation hazard are regarded as supervised, and of A class excavations – as monitored. Moreover, they should be marked with warning signs of radiation and the entrance there should be restricted only to instructed persons.

The decree describes the requirements regarding the monitoring in each class of the danger:

- in excavations of the A class of the radiation danger, the monitoring of the work environment and individual doses of employees employed there is required
- in excavations of the B class of the radiation danger, the monitoring of the work environment and individual doses of employees representative for a given work-place.

The procedure of measures, evidence of results and estimating the level of the danger are described in the annexes to the decree.

The decree demands that measured values were determined by a laboratory accredited on the basis of regulations on accreditation and certification. It means that determinations are prepared according to the standard PN-EN ISO/IEC 17025:2001 concerning the quality system and in accordance with European requirements.

It is required that persons supervising the monitoring of the radiation danger and employees taking measures in excavations were trained in an adequate scientific unit on the basis of a programme approved by the President of the National Atomic Energy Agency in agreement with the President of the State Mining Authority.

Also, the basic prevention rules concerning natural sources of the radiation danger in mines are given in the decree.

The natural radionuclides in the environment

The *Nuclear Law* requires estimating the radiation danger and radiological situation of the country. Such estimation should also include natural radionuclides that radiating concentrations were modified as a result of a human activity. The President of the National Atomic Energy Agency, who is responsible for the estimation, is allowed to use databases of every subject collecting such information. Also, he has to his disposal the network of detecting stations of radioactive contamination and units measuring such contamination. These units are directed mostly to measure artificial radionuclides, discharged to the atmosphere as the result of radiation incidents. Moreover, specialised units are obliged to measure natural alpha- and beta-radioactive isotopes in environmental probes.

Also, there are regulations concerning the content of natural radionuclides in drinkable water and mineral waters.

There are no specific demands for drinkable water as regards the content of each radionuclide except for the tritium ^{3}H. The maximum content of the tritium in drinkable water equals 100 Bq/l. The limit of the content of all radionuclides was described as the total acceptable dose which is 0.1 mSv/year. According to requirements of the nuclear law, it should be the value over the natural background.

As regards mineral, spring- and table waters, the limits for radionuclides were set as the maximum concentrations of the total alpha radioactivity (0.1 Bq/l) and the total beta radioactivity (1 Bq/l). Moreover, it is demanded to eliminate the radon during the production process.

However, these conditions are difficult to interpret. The presence of radionuclides of natural radioactive series (the radon included) and the potassium ^{40}K will influence the result. According to demands of the nuclear law, the contents of those radionuclides, present in the undisturbed environment or raw water, should be subtracted form the result. The latter requires a separate measure.

In case of mineral waters, it does not seem purposeful to set the limits as total alpha or beta activities. Firstly, alpha emitters belonging to different groups of radiotoxicity may be present in water, and consequently the same activity may cause different dose of radiation received. Secondly, the present capabilities of national laboratories allow determining easily radionuclides in examined environmental probes, irrespective of their radiation.

Radiation hazard in the inhabitancy area

Natural radionuclides in the inhabitancy area may cause the danger because of the content of such substances in building materials or base and because of the presence of the radon in the air in rooms. These problems will be discussed below in details.

Radon hazard in legal regulations in the world

In 1994 in United States the maximum acceptable concentration of the radon ^{222}Rn for persons professionally endangered was established on the level of 370 Bq/m^3 for the time of work of 40 hours weekly. In 1953 International Commission on Radiological Protection (ICRP) set the maximum acceptable radon concentration in the air for the constant danger as 3700 Bq/m^3. Other limits were established in 1959: 11100 Bq/m^3 for 40 hours per week and 37000 Bq/m^3 for 168 hours per week. In 1985 ICRP set the so-called year's intake limits of radon daughters for miners on the level of 3,6 Bqh/m^3 what equals the average equilibrium concentration (EEC) 1800 Bq/m^3 for the time of work of 2000 hours per year.

In several countries, Poland included, limits of the radon hazard for professionals were set in units of the concentration of the potential alpha energy of short-lived radon daughters – microjoules on cubic meter (µJ/m^3). The first reason is the fact that the radon daughters, not the radon itself, are the danger for an organism and the second – changes in a ventilation system, for example, will significantly influence the results and cause that the measures of the radon will not reflect the danger appropriately.

Together with the knowledge of the influence of the radon and its daughters on the lung cancer hazard, the interest in dwelling houses, where we spend much more time than in a work-place, was growing.

The United States were the first country where legal regulations concerning the radon in buildings were introduced. In 1979 limits of the radon concentration for buildings were set in Florida, where phosphates are being exploited, and in Colorado in areas where uranium ores are being mined and processed. The intervention levels were set as follows:

- 74 Bq/m^3 of the equivalent (equilibrium) concentration of the radon* (EEC) in Florida
- 200 Bq/m^3 EEC in Colorado.

In 1979 in Sweden, the Radon Commission was created, soon after scientists from Radiological Protection Institute measured high concentrations of the radon in buildings built on rocks enriched in uranium compounds e.g. on aluminium shales. In 1994 the Swedish limits were set as the average yearly radon concentration and presently equal:

- 400 Bq/m^3 for existing houses
- 200 Bq/m^3 for new ones.

In 1990 the European Commission recommended to introduce the following levels in all member countries:

- 400 Bq/m^3 for existing houses
- 200 Bq/m^3 for newly built.

At present, regulations regarding the acceptable concentrations of the radon in buildings exist in most countries. In different countries the acceptable concentrations of the radon in building are differently defined. The most frequent are:

- advisory (action) level – over which the preventive actions should be taken to reduce the radon concentration in a building;
- intervention (enforced) limit – the radon concentration may not exceed this value, the preventive actions are necessary.

Apart from above, there are other definitions describing different levels of the radon concentration:

- exemption (excluded) level – under that level buildings are excluded form the systematic monitoring;
- investigation level – over that level it is necessary to investigate and explain carefully the given case.

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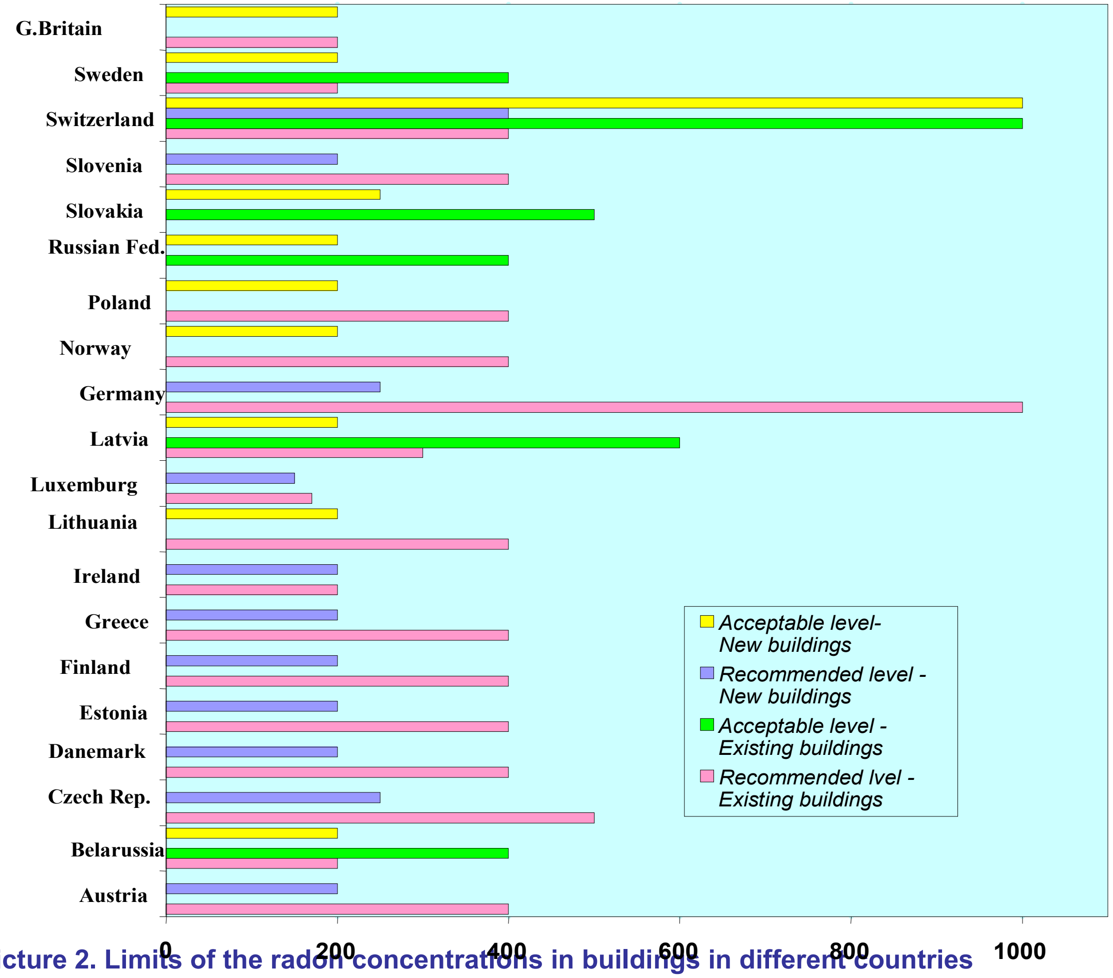
* The equivalent radon concentration EEC – the concentration of the radon being in equilibrium with the radon daughters that is equivalent to the actual concentration of the alpha potential energy when there is no radioactive equilibrium; we get this value from multiplying the radon concentration by the radioactive equilibrium ratio F.

Generally, apart from differences in names, the levels, limits and recommendations are similar in different countries. Usually, in countries where the radon concentrations may vary significantly in buildings because of the complex geological structure, there are several intervention levels differently defined. Commonly, legal regulations define two levels when preventive actions should be taken:

- acceptable (higher) - when it is necessary to undertake urgent preventive actions, usually financially demanding;
- recommended (lower) – referring to buildings where it is possible to reduce significantly the radon concentration using cheap and simple methods.

Figure 2 shows the acceptable concentrations of the radon as regards buildings that already exist and newly built both in EU member countries and other. In most EU countries the limit is lower for new buildings than for older constructions. For the first ones, the acceptable level is 200 Bq/m^3. In Sweden, this level is defined as acceptable, in other countries – as recommended (see the picture). Also, outside EU it was decided that in new building the radon concentration should not exceed 200 Bq/m^3. In Latvia, the acceptable limit equals 300 Bq/m^3. In Switzerland two levels are used: 1000 Bq/m^3 which is acceptable and 400 Bq/m^3 which is recommended.



Picture 2. Limits of the radon concentrations in buildings in different countries

In many non-European countries the limits concerning both new and existing buildings are the same. In United States, for example, the recommended level for new and existing buildings equals 150 Bq/m^3 ; in Canada 800 Bq/m^3; in Australia, Israel and Syria 200 Bq/m^3.

The radiation hazard in buildings in the Polish law

The protection against the ionizing radiation in buildings is described in the Decree of the Minister of Infrastructure of 12 April 2002 *on technical conditions buildings and their location shall meet*. In section 8 chapter 3 titled *Protection against the ionizing radiation and electromagnetic fields* the following requirements are set:

§313.1. A building designed for people or livestock cannot be made from materials and fittings that do not meet requirements of separate regulations on acceptable concentrations and intensities of noxious agents.

2. Yearly average values of the equivalent radon concentration in rooms of a building designed for permanent stay of people cannot exceed the acceptable value set in separate regulations concerning dose limits of the radiation.

The acceptable concentrations and intensities of noxious agents are established by the decree of the Minister of Labour and Social Policy of 29 November 2002; however, these regulations are binding actually only for labour environment. Still, in the first paragraph it is said that in case of the ionizing radiation the dose limits and derivative ratios are established by separate rules. In case of the requirements set in the par. 313 point 1 of the above decree, the separate regulation mentioned there should be the decree of the Council of Ministers of 3 December 2002 *on requirements regarding the content of natural radioactive isotopes in materials used in buildings designed for people and livestock and also in waste materials used in the building industry and monitoring of the content of such isotopes*.

Materials for the building industry are qualified on the basis of two ratios:

$$f_1 = 0,00033 \bullet C_K + 0,0033 \bullet C_{Ra} + 0,005 \bullet C_{Th} ,$$

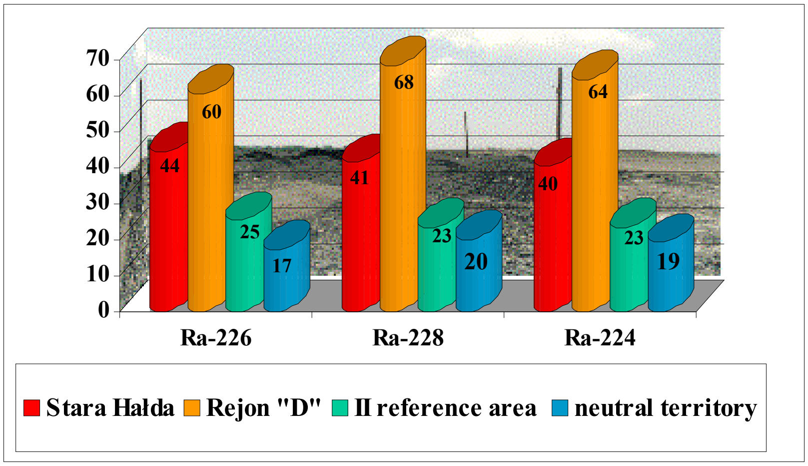
$$f_2 = C_{Ra} ,$$

where:

C_K , C_{Ra} , C_{Th} - concentrations of the isotopes of the potassium ^{40}K, the radium ^{226}Ra and ^{228}Ra.

f_1 ratio defines the content of natural radioactive isotopes in the examined material. **f_2** ratio limits the content of the radium isotope ^{226}Ra because of the danger of the alpha radiation from the radium and its daughters. The first radio is calculated on the basis of concentrations of the activities ^{226}Ra, ^{228}Th and ^{40}K. According to the requirements of the mentioned decree, the values of the activity ratios cannot exceed the following more than 20%:

1. **f_1 = 1 and f_2 = 200** as regards materials used in building designed for people and livestock
2. **f_1 = 1 and f_2 = 400** as regards industrial waste materials used in ground-based buildings erected in urban areas or designed for buildings in a local land development plan and for levelling.
3. **f_1 = 3,5 and f_2 = 1000** as regards industrial waste materials used in ground-parts of buildings not mentioned in the point 2 and to level areas not mentioned in the point 2.
4. **f_1 = 7 and f_2 = 2000** as regards waste materials used in underground parts of buildings, mentioned in the point 3, and underground buildings, rail and road tunnels included, except for waste materials used in underground mining excavations.



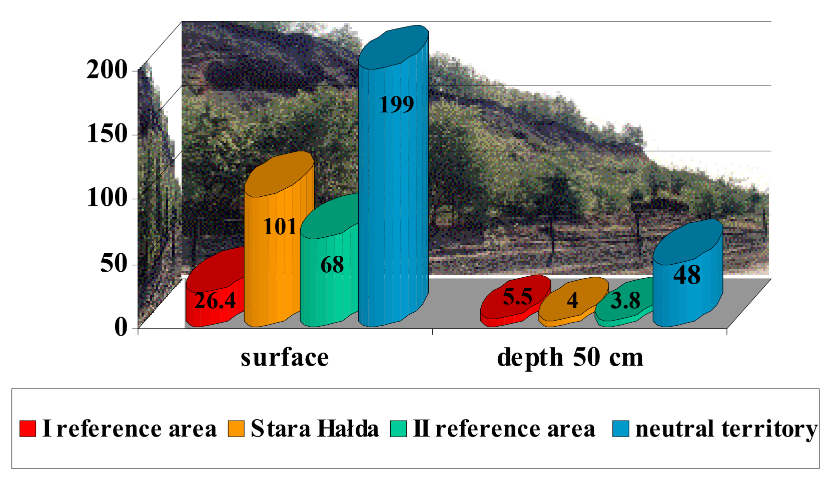
If waste materials are used to level grounds, mentioned in the point 2 and 3, or to build roads, sport and leisure facilities, the absorbed dose on the height of 1 m over the ground, road or facility should be decreased to the value not exceeding 0.3 microgray per hour, observing the f_1 and f_2 ratios.

The requirement to keep the low level of the dose of the gamma radiation in connection with the acceptable concentration of the radium ^{226}Ra may be difficult to meet because we may expect the exceeding of the value of power of the dose even at 650 Bq/kg of ^{226}Ra in the material being used.

Also, the decree describes requirements as regards the quality system of laboratories taking such measures. Nevertheless, it is a pity that it does not refer to the act on accreditation[27] where it is described the procedure of verifying whether the quality requirements are met in laboratories; it has been done in case of mining regulations.

The Instruction no. 234 of the Building Research Institute gives the method of testing the content of the natural radionuclides in building materials. A part of its rules is out-of-date in the light of the decree of the Council of Ministers.

As regards the radon danger in habitable buildings, we need to say that Polish legal regulations have not been adapted to recommendations of the European Union, yet. As far as the point 2 of the mentioned decree of the Minister of Infrastructure is concerned, we should refer to requirements of the decree of the Council of Ministers on dose limits[7]. However, the basic text does not mention the limits of the radon concentration. Only par. 6 item 2 says that the values of dose limits, mentioned in the decree, shall be applied to the increased danger of the natural ionizing radiation, as a result of the human activity. It means the doses from the radon, which concentration in a building is higher that in the environment, should be limited also.



It is said in the annex to the mentioned decree that if the radon nuclides and their daughters, present in the air, are the source of the internal danger, the effective dose is determined by measuring or calculating the alpha potential energy. It is defined there as the total energy of alpha particles emitted during the disintegration of the radon daughters (^{222}Rn) in the radioactive series to the lead ^{210}Pb (with the exception of this nuclide) and the disintegration of the thoron daughters (^{220}Rn) in the radioactive series to the stable lead ^{208}Pb and is given in joules (J). The danger is determined when calculating the concentration of the alpha potential energy in joules by hour per cubic meter (Jhm^{-3}) to the effective dose in sieverts, with the use the following conversion factors:

1.1 Sv/Jhm^{-3} – for the danger from the radon in habitable buildings,
1.4 Sv/Jhm^{-3} - for the danger from the radon at work-places,
1.5 Sv/Jhm^{-3} - for the danger from the thoron at work-places.

It means that in habitable buildings the value of the dose limit (assuming that a person spends 80% of the time in the apartment and the equilibrium factor between the radon and its daughters equals 0.5) is reached if the radon concentration in the apartment equals 47 Bq/m^3. The problem is that in Poland doses from the radon and its daughters in habitable buildings are not included – according to the *Nuclear Law* – to dose limits, and there are not any other reference level for the danger of the radon and its daughters in administrative regulations.

In 1998 the Instruction no. 352/98 of the Building Research Institute was issued, titled *Methods and conditions of taking measures of the radon concentration in the air in rooms of buildings designed for permanent stay of people.* It gives the details of how to chose rooms for the research, which of existing methods may be used for such research and how to prepare documents and reports on measures.

Summary

The amended administrative regulations to the Nuclear Law and Geological and Mining Law put in order the requirements as regards the radiological protection of miners employed in conditions of the increased hazard of the ionizing radiation from natural radioactive substances. However, because of the fact that they have not been issued in the same time, some of their requirements are not clear enough for a user (e.g. the necessity of including doses from the natural background when calculating the danger). Also, some minor misprints can be found in texts of the mentioned decrees.

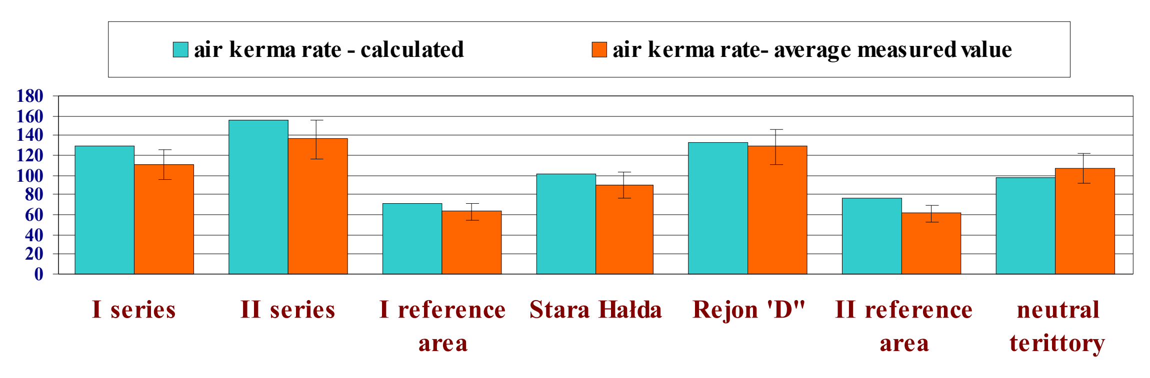
It is much worse in case of managing of waste materials containing higher radioactive concentrations of natural radionuclides that are not classified as radioactive wastes yet. It concerns in particular masses of soil or rock, removed or displaced because of an investment or exploitation of minerals, together with processing. Indeed, it is a loophole in the nuclear and environmental legal regulations.

The regulations of the nuclear law, specifically the decree on radioactive wastes[10], as regards materials containing natural radionuclides, describes only in par. 4 what **is not a radioactive waste**. For example, if the radioactive concentration of the ^{226}Ra isotope in mining sediments does not exceed 100 kBq/kg, such sediments are not radioactive wastes, according to the nuclear law. So, the specific procedure, described in the mentioned decree, is not required.

But regulations concerning the environment protection do not mention the ionizing radiation any more. The act on wastes[17] is an example. In annexes to that act, the radioactivity is described neither as a constituent nor as a property of wastes that demands to classify them as dangerous. It means that disposing of the waste to the environment, even if they contain natural radioactive isotopes of the concentrations increased so much that doses they induce would be close to limit ones or even exceeding them, still is not regulated legally although it may lead to the increase of the danger of the ionising radiation in areas where they are produced, stored or utilized.

It is necessary to regulate urgently the procedure of utilizing the TENORM waste, what means containing higher concentrations of natural radionuclides – as a result of the human activity.

Literature:



Information of the National Atomic Energy Agency on the state of nuclear security and radiological protection in Poland in 2001. Bezpieczeństwo Jądrowe i Ochrona Radiologiczna, 2 (50), 2002 (in Polish)

Nuclear Law Act, 10 April 1986. Dziennik Ustaw No. 12, item 70 with the subsequent changes (in Polish)

International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources. FAO, IAEA, ILO, OECD, PAHO, WHO 1994.

EU Council Directive 96/29/Euroatom „The EC Basic Safety Standards”.

Recommendations for the implementation of Title VII of the European Basic Safety Standards Directive (BSS) concerning significant increase in exposure due to natural radiation sources. European Commission, Radiation Protection 88, 1997

Act of 29 November 2000 on *Nuclear Law*, Dziennik Ustaw 2001, No. 3, item 18 with subsequent amendments (in Polish)

Decree of the Council of Ministers of 28 May 2002 on dose limits of the ionizing radiation, Dziennik Ustaw No. 111, item 969 (in Polish)

Decree of the Council of Ministers of 3 December 2002 on documents required when applying for the permission for activity connected with the hazard of the ionizing radiation or when registering such activity, Dziennik Ustaw No. 220, item 1851 (in Polish)

Decree of the Council of Ministers of 17 December 2002 on specific conditions of the safe work with sources of the ionizing radiation, Dziennik Ustaw No. 239, item 2029 (in Polish)

Decree of the Council of Ministers of 3 December 2002 on the radioactive waste and burnt nuclear fuel, Dziennik Ustaw No. 230, item 1925 (in Polish)

Decree of the Council of Ministers of 6 August 2002 on basic requirements regarding monitored and supervised areas, Dziennik Ustaw No. 138. item 1161 (in Polish)

Decree of the Council of Ministers of 6 August 2002 on types of work-places of the great importance for the nuclear safety and radiological protection, specific conditions and procedure of granting the rights of a inspector of the radiological protection, Dziennik Ustaw No. 145, item 1217 (in Polish)

Decree of the Council of Ministers of 5 November 2002 on requirements regarding recording of individual doses, Dziennik Ustaw No. 207, item 1753 (in Polish)

Decree of the Council of Ministers of 23 December 2002 on requirements regarding dosimetric devices, Dziennik Ustaw No. 239, item 2032 (in Polish)

Decree of the Council of Ministers of 23 December 2002 on emergency procedures in case of radiation incidents, Dziennik Ustaw No. 239, item 2033 (in Polish)

Decree of the Council of Ministers of 6 August 2002 on the cases when the activity connected with the hazard of the ionizing radiation is not the subject of duty of obtaining the permission or registration and cases when it may be performed on the basis of the registration, Dziennik Ustaw No. 137, item 1153 (in Polish)

Act of 27 April 2001 on the waste, Dziennik Ustaw No. 62, item 628 (in Polish)

Polish Standard PN-89/Z-70071 Radiological protection in underground mines. Limits of the exposure of miners to natural radioactive isotopes and methods of monitoring (in Polish)

Instruction of monitoring of the radiation hazard of natural radioactive substances in coal mines. Wspólnota Węgla Kamiennego (Coal Mine Community), Katowice 1988 (in Polish)

Guidelines for the classification of mining excavations and safe work in conditions of the radiation hazard caused by natural radioactive substances. Wspólnota Węgla Kamiennego (Coal Mine Community), Katowice 1988 (in Polish)

Act of 4 February 1994 Geological and Mining Law, Dziennik Ustaw No. 27, item 96 with subsequent amendments (in Polish)

Ordinance of the President of the State Mining Authority of 3 August 1994 on criteria of natural dangers assessment and the procedure of including mine deposits, their parts or mine excavations to the appropriate class of danger. M.P. No. 45, item 368 (in Polish)

Decree of the Minister of Industry and Trade of 14 April 1995 on the industrial safety, work performing and technical fire protection in underground mines, Dziennik Ustaw No. 67, item 342 (in Polish)

Act of 27 July 2001 changing the Geological and Mining Law, Dziennik Ustaw No. 100, item 1190 (in Polish)

Decree of the Minister of Interior and Administration of 14 June 2002 on natural dangers in mines, Dziennik Ustaw No. 94, item 841 (in Polish)

Decree of the Minister of Economy of 28 June 2002 on the industrial safety, work performing and technical fire protection in underground mines, Dziennik Ustaw No. 139, item 1169 (in Polish)

Act of 30 August 2000 on the system of the consistency assessment, Dziennik Ustaw No. 166, item 1360 (in Polish)

Polish Standard PN-EN ISO/IEC 17025:2001 General requirements regarding competencies of research and standardization laboratories (in Polish)

Decree of the Council of Ministers of 17 December 2002 on stations of early detection of the radioactive contamination and centres for measures of the radioactive contamination, Dziennik Ustaw No. 239, item 2030 (in Polish)

Decree of the Minister of Health of 19 November 2002 on requirements regarding the quality of the drinkable water for people, Dziennik Ustaw No. 203, item 1718 (in Polish)

Decree of the Minister of Health of 27 December 2000 on specific conditions and sanitary requirements in production of natural mineral waters, natural spring waters and table waters in unit packages, Dziennik Ustaw No. 4/2001, item 38 (in Polish)

Commission Recommendation of 21 February 1990 on the protection of the public against indoor exposure to radon. European Communities. 90/143/Euratom

Decree of the Minister of Infrastructure of 12 April 2002 on technical conditions buildings and their locations shall meet, Dziennik Ustaw 75, item 690 (in Polish)

Decree of the Minister of Labour and Social Policy of 29 November 2002 on the highest acceptable concentrations and intensities of noxious agents in the environment of work, Dziennik Ustaw No. 217, item 1833 (in Polish)

Decree of the Council of Ministers of 3 December 2002 on requirements regarding the content of natural radioactive isotopes in materials used in buildings designed for people and livestock and also in waste materials used in the building industry and monitoring of the content of such isotopes, Dziennik Ustaw No. 220, item 1850 (in Polish)

Instruction no. 234/95 *Guidelines for research of the natural radioactivity of raw materials and building materials*, Building Research Institute, Warsaw 1995 (in Polish)

Instruction no. 352/98 *Methods and conditions of taking measures of the radon concentration in the air in rooms of buildings designed for permanent stay of people*, Building Research Institute, Warsaw 1998 (in Polish)

NORM IN MINING INDUSTRY IN POLAND

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[2]State Mining Authority, Katowice, Poland

ABSTRACT

The main branches of Polish mining industry are the coal, copper, zinc and lead, salt and oil and gas mines. In many of these mines the problem of the naturally occurred radioactive materials is present.

The main source of risk for the miners is due to the short-lived radon daughter products present in air. This source of risk is present in all Polish underground mines. In coal, copper and oil and gas mines the radium-bearing waters are present. This is a potential risk for the miners, but for the environment too, because all mine water is pumped out to the rivers. In coal and copper mines radium precipitates from the waters creating the risks of the internatal conatamination but of external gamma radiation too.

The Polish *Geological and mining law* needs to perform monitoring of all sources of natural radiation at the workplaces and to introduce the preventive measures, if necessary. In this paper the results of the monitoring and prevention measures are described.

INTRODUCTION

Exposure to ionising radiation is usually treated by members of general public in Poland as a phenomenon related with nuclear power plants and/or disasters in nuclear installations. The best example was Polish Atomic Law [1], focused till early 90's exclusively on nuclear safety, application of artificial sources of radiation and nuclear accidents. Lately more and more attention is paid to radiation exposure caused by natural radioisotopes. In last several years broad investigations in this field are connected not only with radon exposure in dwellings but also with radiation hazard at workplaces and contamination of the natural environment, caused by non nuclear industries. It has been reflected in the novel of the Atomic Law [2], prepared by Polish Parliament to harmonise Polish regulations with European Union standards [3].

Up to now the specific information on levels of natural radioactivity in waste materials and by-products, created by different branches of Polish industry, are scarce. Therefore it is very difficult to assess the influence of natural radionuclides on exposures at workplaces and pollution of the environment. Only in the hard coal mining the situation is more clear and the better recognised. In this paper we would like to describe the state of the knowledge, concerning this problem in Poland. Results of investigation in exploitation industry will be shown (hard coal mines, copper ore mines, lead and zink mines and salt mines) as well as data from processing industries (dealing with fertilisers, power generation and production of construction materials).

In first part of the paper results of measurements of the most important natural radionuclides (^{226}Ra, ^{228}Ra and ^{40}K) in different materials are gathered – raw materials, waste and by-products, produced or dumped into natural environment. In the second part the assessment of the doses for workers, exposed to sources of natural radiation in different branches of industry, will be done.

1. NATURAL RADIOACTIVITY OF RAW MATERIALS AND INDUSTRIAL SPOILS

In table 1 the main branches of the exploitation industry in Poland are shown. The annual production of raw materials is of about 219 mln tonnes [4]. Moreover, roughly 82 mln tonnes of solid spoils is dumped onto the surface per year. Additionaly, about 2,9 mln cubic meters of waste water is pumped out daily [16].

The production of phosphate fertilisers is based on imported phosphates (slightly more than 0.5 mln tonnes per year). Waste materials, generated in power industry, must be also taken into account – of about 13 mln tonnes annually.

There are no complete data of natural radioactivity of raw and waste materials in mentioned above branches of industry. The most reliable results come from mining industry, because investigations in that filed have been performed in hard coal mines, metal ore mines and other underground mines since 30 years. At the end of 80's in whole underground mining the system of radiological protection against natural radionuclides has been implemented. At the beginning of 90's requirements of radiological protection in mines has been issued as the Decree of Polish Parliament [5].

Table. 1. Production of raw and waste materials in Poland

Branch of the industry	Production, mln tonnes/year	Solid waste, mln tonnes/year	Liquid waste, mln m^3/daily
Coal mining	112	40	0,58
Copper ore mining	28,4	25	0,06
Lead and zinc mining	5	4	0,44
Limestone quarries	8	3	0,50
Salt mines	4,2	10	0,16
Lignite open pit mines	60,8		1,26
Oil	0,4		0,0004

Systematic obligatory measurements enabled to gather a broad database of results of concentrations of natural radionuclides in air, water and solid materials not only in underground galleries but also in the natural environment in the vicinity of mines. The most complete database exists for hard coal mining industry (see table 2) [6,7]. Fewer data have been gathered for copper ore mines (table 3) and lead and zinc mines (table 4). Additionally, in table 5 results from salt mines are presented. Table 6 contains data for waste materials from oil and gas mining industry.

Accordingly to the presented data, in almost all raw materials, produced by Polish mining industry (like metal ores and hard coal), typical concentrations of natural radionuclides are low. Nonetheless, in some cases we observe radium concentrations above value 50 Bq/kg, quoted in UNSCEAR reports as the upper limit for the Earth's crust.

Table. 2. Maximum concentration of radionuclides in different product of hard coal mining industry [8,9,10,18]

Product	Ra-226	Ra-228	K-40
Hard coal, Bq/kg	159	123	785
Waste rocks, Bq/kg	122	106	1797
Underground scales, precipitated out from waste waters, Bq/kg	204127	83785 (215486)	14815
Brines, kBq/m^3	391	99	-
Scales, precipitated out on surface, Bq/kg	156942	83785	15243
Settling ponds, water, kBq/m^3	7,6	4,4	-
Settling ponds, sediments, Bq/kg	104067	83785	-

Table. 3. Maximum concentration of radionuclides in different product of copper ore mining industry [9,11,12,17,18]

Product	Ra-226	Ra-228	K-40
Copper ore, Bq/kg	75	20	466
Concentrated ores after flotation, Bq/kg	145	20	688
Waste rocks, Bq/kg	53	43	676
Waste products from flotation processes, Bq/kg	98	39	1243
Scales, precipitated out from waste waters, Bq/kg	1340	68	1108
Copper slag, Bq/kg	530	183	1459
Brines, kBq/m^3	95	12	-

Table. 4. Maximum concentration of radionuclides in different product of zinc and lead ore mining industry [9,13]

Product	Ra-226	Ra-228	K-40
Zinc ore, Bq/kg	21	17	65
Waste rocks, Bq/kg	40	17	194
Waste products from flotation processes, Bq/kg	26	16	80
Scales, precipitated out from waste waters, Bq/kg	76	61	
Brines, kBq/m^3	0,5	0,1	-

Table. 5. Maximum concentration of radionuclides in different product of salt mining industry [9]

Product	Ra-226	Ra-228	K-40
Brines, kBq/m^3	0,3	0,5	-

Table. 6. Maximum concentration of radionuclides in oil and gas mines

Product	Ra-226	Ra-228
Brines, kBq/m^3	258,1	22,8

Quite opposite is the situation of waste products, especially from mining industry. Upper Silesian Coal Basin has rather specific geological and mining conditions, therefore inflows of brines with high radium content into underground galleries are numerous. De-watering of mines (removal of these brines from mines onto the surface and further to rivers) causes the contamination of the natural environment in the vicinity of coal mines. Sometimes in these brines not only radium bat barium ions are present and then radium co-precipitates with barium in form of highly radioactive scales. Such processes can be observe not only in the underground workings, but also sometimes on the surface, in settling ponds or rives, mainly in cases, when wastewaters have been not treated before dumping into rivers. Such contamination of the environment is a potential source of radiation hazard not only for miners but also for the inhabitants of adjacent lands. Similar problems have been found in copper ore mines and in their vicinity.

2. RADIATION HAZARD AT WORKPLACES

Occurrence of natural radionuclides at workplaces is the source of the radiation hazard for workers. The most important natural radionuclide is obviously radon and radon progeny, while other sources are: external gamma irradiation or accidental ingestion and inhalation of long lived nuclides. In Polish mining industry monitoring of all possible sources of expose at workplaces in underground galleries is obligatory, but in other branches such measurements have been done only occasionally.

In following tables results of assessment of dose equivalents in different branches of industry has been presented – for coal mining, copper ore mining, lead and zinc mining and in phosphate fertilisers industry. The assessment is done for the exposure from radon progeny, gamma rays and internal contamination.

Table. 7 Maximum dose equivalents in coal mines (1995-2003) [7]

Source of hazard	Dose equivalent, mSv/year
Radon progeny	7,2
Gamma dose	1,8
Internal contamination, radium isotopes	4,2

Table. 8 Maximum dose equivalents in metal ore mines [7,15]

Source of hazard	Dose equivalent, mSv/year
Radon progeny	9,6
Gamma dose	0,08

Table 9. Maximum doses in phosphate industry [14]

Source of hazard	Dose equivalent, mSv/year
Radon progeny	0,18
Gamma dose	0,35

3. SUMMARY

Worldwide the exposure to radon progeny is usually treated as the only one source of radiation hazard at workplaces. The same situation can be observed in Polish exploitation and power generation industry, except underground mining. Due to high concentration of radium isotopes in brines and co-precipitation of radium and barium as highly radioactive scales, the gamma radiation and internal contamination could be important source of hazard. Additionally, the release of radium bearing waters and deposits leads also to the contamination of the natural environment in the vicinity of mines. The pollution may cause the increase of the exposure for the inhabitants of adjacent lands. The maximum dose equivalents for the members of the Upper Silesian population have been calculated at the level of few mSv per year.

References

- Atomic law, Dz. U. Nr 12, poz. 70, 1982 (in Polish)
- Atomic Law. Dz.U. nr 3, poz. 18, 2000 (in Polish)
- EU Council Directive 96/29/Euroatom „The EC Basic Safety Standarts”
- Statistical yearbook 2000. GUS, Warszawa, 2001
- Geological and mining law, 1994 (in Polish)
- Skowronek J.: Radiation exposures to miners in Polish coal mines. Radiation Protection Dosimetry, vol. 82, No 4. Pp. 293-300 (1999)
- Skowronek J.: Annual report (2003) on radiation hazard. Central Mining Institute, Katowice, 2004 (in Polish)

- Wysocka M., Skowronek J.: Natural radioactivity of hard coal in Rybnik-Jastrzębie region. Publs. Inst. Geophys. Pol. Acad. Sc., M-15 (235), 1991 (in Polish)
- Databases, Central Mining Institute, Katowice.
- Wysocka M., Skowronek J.: Investigation on the radioactivity of carboniferous strata in Upper Silesia. Central Mining Institute, Katowice, 1988 (in Polish)
- Wysocka M., Michalik B., Stec K. et al.: Changes od radon concentration in relation to mining activity. Central Mining Institute, Katowice, 1997 (in Polish)
- Environment 2000. GUS, Warszawa, 2000
- Girczys J., Skowronek J., Źródłowski B.: Spectrometrical analysis of Zn-Pb ores. Zesz. Nauk. Polit. Śl., seria górnictwo, zesz. 122 (749), 1983 (in Polish)
- Chruścielewski W., Olszewski J., Kamiński Z.: Radiation hazard in phosphate industry. Medycyna Pracy, L, 1999, 5 (in Polish)
- Kluszczyński D., Kacprzyk J.: Estimation of radon progeny hazard in metal ore mines. Raport IMP, Łódź, 2001 (in Polish)
- Report on mine waste waters. State Mining Authority, Katowice, 2001 (in Polish)
- Muras K., Olszewski J.: Determination of natural ionizing radiation exposure in the surroundings of copper mines in Poland. Medycyna Pracy, XLIV, 1993, No 4
- Michalik B., Skubacz K., Skowronek J., Mielnikow A.: Statistical analysis of TENORM In Polish industry. Interim report of EU project TENORMHARM. Deliverable No 6, 2003.

THE ASSESSMENT OF EXPOSURE TO IONISING RADIATION AT SPOIL BANKS

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Introduction

Mining activity leads to two different scenarios where occurrence of diverse waste results in enhanced radiation risk to workers and members of the public. In the first one the radium bearing brines discharged from mines into surface waters and precipitated from them sediments have to be taken into consideration. The second scenario encloses all kind of gangue (waste rocks) extracted with hard coal. The radionuclide concentration in this kind of waste is not found to be so high, but it is very often higher than average concentrations in soil on the surface.

The phenomenon of the radioactivity of saline waters from coal mines in Poland was discovered in the 1960’s [Sałdan, 1965]. Later, investigations showed that radium concentration in water was correlated with the salinity [Tomza & Lebecka, 1981]. In some cases, the total dissolved solids concentration (TDS) exceeds 200 kg/m^3, whilst the radium concentration may reach 400 kBq/m^3. The analysis of radium isotopes in underground inflows showed that the total (in all currently working collieries) input of ^{226}Ra was about 725 MBq per day, while the corresponding value for ^{228}Ra was roughly 700 MBq per day [Wysocka et al., 1996]. In coal mines two types of brine were distinguished. In type called “A” ions of barium and radium are present, while in type “B” only radium ions and sulphate occur [Lebecka et al., 1986]. From type “A” of waters radium isotopes easily precipitate out with barium carrier as sulphates after mixing with waters rich in sulphate ions. In case of type “B” of radium-bearing waters precipitation does not occur due to the lack of the barium carrier. From such waters radium is removed in a slow process of sorption on bottom sediments. These two processes are the source of sediments with enhanced radium content [Michalik et al., 1995]. Owing to local hydro-geological conditions less than a half of the total yearly amount of radium remains in the underground galleries whilst about 60% are transported with pumped water to settling ponds on the surface. [Lebecka et al., 1993]. The main task for these ponds is to clear underground waters from suspended matter before discharging to rivers. By the way, depending on the dimensions of the settling ponds and their retention periods a certain part of radium carried with water is deposited together with the suspended matter on the bottom and banks. Amount of deposited sediments depends on the type of the water. In case of water type “A” it can be up to 90% thought in case type “B” it is only about 7%. The mass specific activity of radium isotopes, in these sediments may sometimes reach 400 kBq/kg [Michalik et al. 1995] so that they constitute an important source of contamination of the natural environment in surrounding area. In spite of precipitation and sorption, the significant part of radium is released into rivers. The majority of Polish hard coal mines lay on river basins of the Oder and the Vistula, this leads to enhanced concentration of radium in these rivers, even several tens of kilometres from the point of mining water discharge [Michalik et al.1999].

The radiation risk to members of the public caused by these phenomena, in spite of very wide range of observed mass specific activity of radium in the sediments, is rather low. Currently all the settlings ponds lay on the areas that belong to particular collieries. Access to these areas are restricted to authorised personnel this is why the potential exposure to external radiation is limited only to staff engaged in certain practices and ultimately, controlled in the frame of occupational risk monitoring. Additionally, during normal exploitation, settling ponds are filled with water that constitutes a cover against external radiation from the bottom sediments. A serious problem will emerge in the near future when the mines will be closed. Up to now, the inventory of all interesting settling ponds (from the radiological point o view) was prepared [Michalik et al. 2002].

The second kind of waste produced by hard coal mining differs from the first one in the total amount and mass specific activity of particular natural radioactive isotopes. This kind of waste consists of diverse rocks, which have been extracted together with hard coal.

Hard coal exploitation has lasted on the Upper Silesian Coal Basin since the 16th century and the average yearly production of coal after II World War was about 100 millions tons. These facts show that it is no so easy to find on this territory a place that has not been affected by the mining activity. Up to 20% of the Upper Silesian conurbation's surface is covered by waste material originating from collieries. The current production of hard coal (about 80 mln. tons per year) causes the emergence of few square kilometres of new spoil banks each year.

The radionuclide concentration in this kind of waste is not found to be so high, but it is very often higher than average concentrations in soil on the surface. Though the specific mass activity of the certain natural radioactive isotopes in waste rocks is merely few times much more than in surrounding area, taking into account that Upper Silesia is densely populated, related radiation risk can be significant from radiological point of view. In comparison with the risk caused by the sediments, this potential risk had been considered as not worth enough to devote any efforts for assessment. This approach to this phenomenon led to the lack of reliable data, resulted in that waste rock heaps sometimes are deemed by members of the local society to be as dangerous as radioactive waste.

Sites of investigation

The waste rocks from hard coal industry generally consist of two categories created during different stages of coal exploitation. The first one, gangue, is created during driving shafts and underground galleries. This category contains all kinds of carboniferous rocks. The second one is constituted by tailings from coal cleaning sub-processes as coal wet or dry cleaning, jigging, sink-float. This category contains mainly carboniferous argillaceous rocks originating from floor or roof and interlayer.

During the whole process of exploitation chemical properties of this kind of waste never been changed and any sub-process could not lead to exchange of matter with surrounding area. Then, potential enhanced radiation risk is directly related only to their primordial properties resulted from geological origin of rocks that constitute the waste. Therefore, in order to carry out the radiation risk estimation properly, two different mining regions have been chosen for survey. Coal seems, exploited in these regions, lie on different carboniferous systems then properties of the rocks occurring together with coal differ from each other.

Table 1. Geological characteristic of mining region chosen for investigation

	area I	**area II**
Chronostrati-graphical classification	Crakow Sandstone Series	Uppersilesian Sandstone Series
Beds	Łaziska and Libiąż Beds	Orzesze, Załęże, Ruda Beds
Petrgraphical composition	Sandstone (variable-graded), Arkose-sandstone, Siltstone, shists, silstone	Siltstone, siltstone-coal shists
Mineralogical composition	Quartz, kaolinite, chlorite, pyrite	Calcite, siderite, dolomite

On these regions the measurements of radiation risk were carried out on three waste rock piles that vary in age and stage of restoration. For comparison, the same measurements were done respectively on neighbouring rural areas where, according to available information, any kind of waste has never been stored. These sites were named *reference* area II and I (photo 1). In order to create additional possibility of comparison one more territory was chosen. There was a military training area lying far from investigated mining areas in neighbouring province. This region had never been subjected to any kind of mining activity. For purpose this work the site was termed *neutral territory.*

The first area of investigation, was located close to town Bieruń where the waste rocks were used as landfill of ca 13 hectares territory (photo 2 & 3), that had collapsed due to underground mining activity. About 1.5 million of cubic meter of waste rock will have been used for this purpose. About two third derived from a coal clean process. The remaining part consisted of gangue. This area was earmarked as a recreation park for local society. In this case, *two series* of measurements were carried out. The first one was done on the part of this territory that was just after initial biological land reclamation. The second one was performed on the part that was still under exploitation and fresh waste rocks were being dumped on it.

The second area of investigation lay on the district of the town Rybnik. In this case two completely different objects were chosen. The first one called *Stara Hałda* (photo 4) was an old waste rock heap. Its exploitation was finished in 1950. In the course of time the process of self-reclamation went on and now this heap is overgrown with few-meters-high birches (photo). This heap contains about 0.6 million cubic meters of waste rock, mainly burned carbonaceous shale, and occupies 6-hectares surface. The second site where investigations were done, in comparison to the first one, was a quite new. It was the waste rock dump, called *Rejon D* (photo 5) that had been being exploited for few years, then was prepared for land reclamation. The surface of this waste dump was about 16 hectares.

The altitude of all investigated sites, including reference areas and neutral territory, was between 200 and 300 meters.

Risk factors and measurements methods

For adequate risk assessment the following factors of radiation risk were taken into consideration:

Mass specific activity of radium isotopes, respectively Ra-226 from uranium decay series and Ra-228 from thorium decay series, and last but not least K-40 isotope of potassium. All mass specific activities were determined by high-resolution gamma spectroscopy with germanium detectors and GENIE 2000 software from Canberra. The concentration of radium 226 was measured basing on 186.2 keV energy line, radium 228 through actinium 228 and potassium K-40 directly from line 1461 keV. The measurement system was calibrated using the set of standard samples. Standard samples consisted of an adequate carrier with very low activity and known amount of a reference material. All substances used for the carriers had been pre-screened for gamma-emitting radionuclides. IAEA Gamma Spectrometry Reference Materials: RGU-1, for uranium series, RGTh-1 for thorium series and RGK-1 for potassium were used for efficiency calibration. The efficiency curve was calculated basing on standard samples for each detector. It was very important that as basic points for efficiency calculation were taken into account only the lines derived from radionuclides whose mass specific activity had been being intended to measure in waste rock and environmental samples. The total uncertainty, at one sigma level, was in each case less than 10% and minimum detectable activity for particular, determined isotope was less than 1 Bq/kg.

Measured samples were crushed and sieved to grain size of smaller than 2 mm. Besides grinding samples were dried in 105 °C to stable mass. Depending on the intended detector, prepared sample was put into relevant measurement container. Three kinds of measurement containers were used that differ from each other in volume. All of them were polyethylene *Marinelli* containers with volume 1, 0.6 and 0.11 litre respectively.

Air kerma free-on-air, K_a, - above the ground was measured by GAMMA-31 dosimeter. The GAMMA-31 dosimeter, around 30mm in diameter, 8mm high and 7 g weight, was equipped with 3 MCP-N thermoluminescence detectors (TLD). These TLD's had been made as sintered discs, about 1mm thick and 4.5mm in diameter. They were built on the base of the LiF luminophore with such dopants as Mg,Cu,P. It was a very sensitive luminophore but required a quite precise annealing process at temperature controlled conditions of 240°C±2°C over 10minutes. Its sensitivity was tens times higher than for the popular LiF:Mg,Ti TLD's. Every GAMMA-31 personal dosimeter was marked with permanent signs and could be used as a personal dosimeter or only as an environmental one. If it is necessary, they could be sealed with lead.

After the TLD's had been annealed according to relevant procedure, the Gamma-31 dosimeter were located on appropriate site for 1-month exposure. After exposure, the GAMMA-31 dosimeters came back to the laboratory where TLD's were read out and calibrated, using certified caesium 137 source. Afterwards air kerma rates were evaluated. Measurement uncertainty at a 95% confidence level, at a dose rate of 0,07 μGy/h and one-month exposure was less than 7%.

Radium isotopes concentration in seepage from the spoil banks and surface waters in their vicinity - was performed by method that enables simultaneous determination of ^{226}Ra, ^{228}Ra and ^{224}Ra [Chałupnik et al. 1993]. Generally, radium was co-precipitated with a barium carrier and lead, then the precipitate was dissolved in EDTA. After that radium was separated from Pb by co-precipitation of Ra and Ba as sulphates at pH=4.5. The Ba and Ra sulphate precipitate was mixed with a gelling scintillation cocktail, which ensured that the precipitation was suspended uniformly in the whole volume of the scintillation cocktail. Afterwards the sample was measured using a low-background Wallac Quantulus 1220^{TM} LS spectrometer that had a heavy

Pb shielding, low radioactivity of selected construction materials, an anticoincidence guard, a sophisticated spectrum analyser and a pulse-shape analyser, which enables distinguishing α and β particles.

For a sample prepared from 1 litre of water, and with two 1-h measurements, the low limits of detection at confidence level 0.95 was as follow:

^{228}Ra = 20 Bq/ m^3
^{224}Ra = 20 Bq/ m^3
^{226}Ra = 3 Bq/ m^3

Radon concentration in soil gas – was determined by alpha radiometer RGR equipped with additional photomultiplier enabling read-out of Lucas cells. The soil gas samples were taken by special pipe from approximately one-meter depth. Radon concentration was evaluated by counting rate obtained 3 hour after sampling. The applied method enabled to assess radon concentration in soil gas with quite good uncertainty less than 15 % and low limit of detection about 12 Bq/m^3.

All applied measurement method was certified in 1993 year by Polish Centre for Accreditation [Mielnikow et al. 1996].

Determination of the mass specific activity of particular radionuclides and their distribution in waste or soil enables me to calculate the value of dose rate (or air kerma free on air) above the ground. Therefore, having the results of direct measurements of this quantity it was possible to make a comparison, distinguish and then exclude the contribution to the total value of this quantity originating from agents that are not related directly to properties of waste rock, for example: caesium fall-out or cosmic radiation. This approach lets me make a clear assessment of potential increment of risk caused by external radiation on a waste rock pile. Additional information about remaining factors, namely radium concentration in surface water permeating the heaps, radon concentration in soil gas and finally, stone dust concentration in the ground layer of atmospheric air, will complete the estimation of total radiation risk.

Sampling

Taking into consideration that contribution to gamma dose rate coming from source of radiation lying further than 10 meters from a detector is negligible [ICRU 53] had been assumed that distance between sampling point should not be longer than 20 meters. According to this and local conditions sampling points were placed along a straight line crossing the waste dump or in a grid covering a relevant part of the investigated site. In each point three Gamma-31 detectors were exposed at 1, 2 and 3 meters-level above the ground. The samples of waste or soils were taken from surface and from 50-cm depth. In majority of the sampling points radon concentration in soil gas was double-checked especially at sites where ground's permeability was very low. Samples of water were taken twice from small streams that are fed mainly by rainwater infiltrating the spoil banks, during summer and autumn. Finally, 190 samples of waste rocks and soil were taken, 306 Gamma-31 detectors were exposed, about 500 individual measurements of radon concentration in soil gas were done and 26 samples of water were analysed.

Specific mass activity and dose from external exposure to gamma radiation

The result of gamma spectroscopy analysis suggested that the concentration of natural radionuclides in samples collected on the surface does not differ from that were taken from half-meter depth. For verification the hypothesis that average value of natural radionuclides concentration in particular layers were equal the statistical *test t* was applied. The obtained results proved that, besides one small part of the first site of investigation, where land reclamation had been carried out, a homogenous distribution of radionuclides in waste and soil could be assumed. So that in cases of radium and potassium isotopes the average value of concentration was calculated. These are presented in figures 1-4.

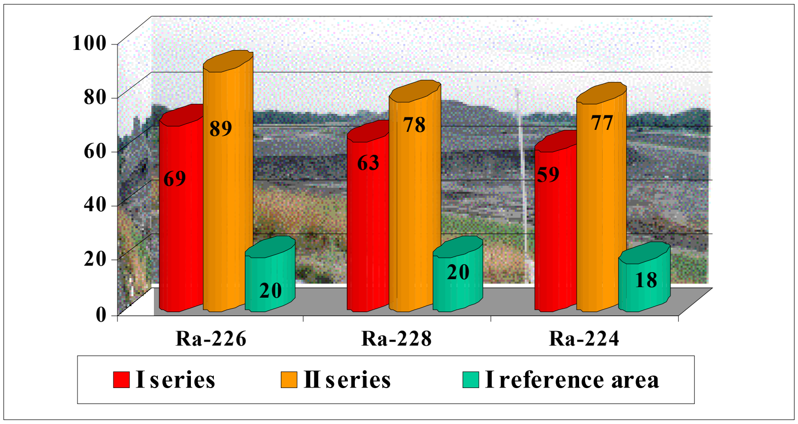

Fig.1 Specific activity of waste rocks and soil from the first area of investigation, [Bq/kg]

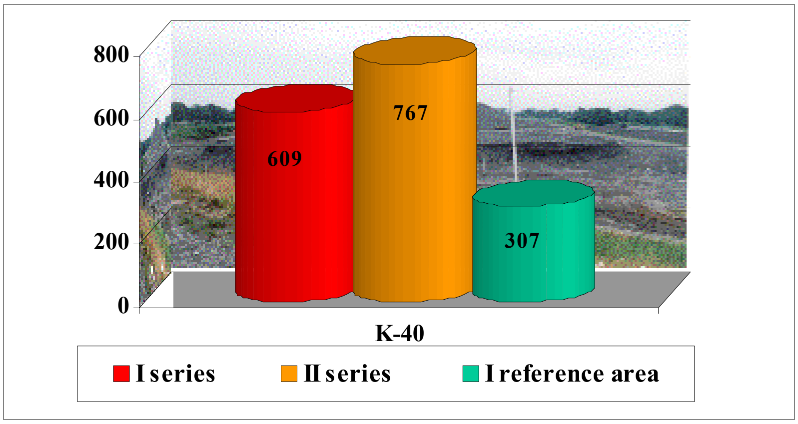

Fig.2 Specific mass activity of waste rocks and soil from the first area of investigation, [Bq/kg]

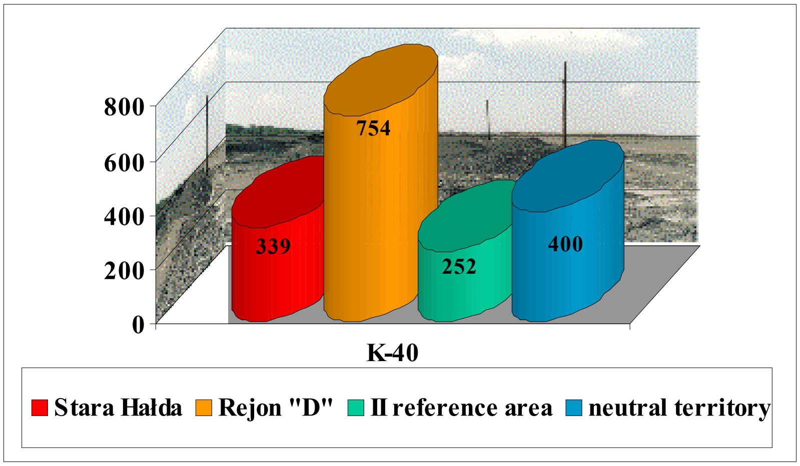

Fig.3 Specific mass activity of waste rocks and soil from the second area of investigation, [Bq/kg]

Fig.4 Specific mass activity of waste rocks and soil from the second area of investigation, [Bq/kg]

The average activity concentration of measured radium isotopes in samples of waste rocks was a bit higher than in samples from the reference areas and neutral territory. The biggest difference occurred in case of the first site of investigation where the mass specific activity of radium 226 was four times higher than in relevant reference area. The smallest one was observed on the Stara Hałda, where, probably owing to a soil-creation process has been lasting for several years concentration of radium isotopes was diluted. Differences in K-40 concentration were not so high and do not exceed the upper limit of the range reported as typical for earth crust [UNSCEAR, 1982].

In case of caesium the situation was completely different. All waste rocks, extracted from underground after Chernobyl disaster are generally not affected by radioactive fall-out. Only very small amount of caesium has been deposited on the surface of

Stara Hałada due to precipitation or dustfall. On the contrary, the concentration of caesium in samples taken from reference areas and, especially, from neutral territory was quite high and strongly depended on depth. The results of caesium's 137 isotope mass specific activity measurements are presented in figure 5.

Fig.5 Specific activity of caesium in waste rocks and soil the second area of investigation, [Bq/kg]

Basing on measured mass specific activity the contribution of each constituent to total air kerma rate above the ground would be calculated. For this purpose the following assumptions were made:

- Natural uranium and thorium series are in secular equilibrium. This fact was proved by measurement particular elements and isotopes included in uranium and thorium series, respectively: Bi-214, Pb-214 and Ac-228, Pb-212, Bi-212, Tl-208.
- The average energy gamma radiation for particular series was respectively 504 keV for uranium series and 550 keV for thorium series. Taking into account the rate activity concentration of radium 226 to radium 228, contribution of energy 1460.75 keV from K-40 and, where it was necessary, energy 661 keV from caesium, the average energies for all investigates sites varied in range 530 - 545 keV.
- The good enough approximation of the radiation source distribution is that of an infinite half space with a homogenous source concentration in the horizontal plane and where possible variations occur only with depth in soil or waste. For natural radionuclides, as it had been proved, the uniform activity concentration distribution with depth was true. For caesium the model of decreasing exponential profile with depth was considered as the best.

- For the component coming from radionuclides occurring in ground-level atmosphere, namely: radon isotopes and their progeny and beryllium, the simplest model, basing on a semi-infinite cloud with uniform distribution in air was used.

Then the component of total kerma rate caused by natural radionuclides was calculated using following coefficient recommended by ICRP [ICRP Report, 53] :

0.462 [μGy × h^{-1}/Bq × g^{-1}] - for uranium series,
0.604 [μGy × h^{-1}/Bq × g^{-1}] - for thorium series,
0.0417 [μGy × h^{-1}/Bq × g^{-1}] - for ^{40}K.

Table 3. Theoretically calculates contribution of natural radionuclides to the total air kerma rate 1 meter above the ground level.

Site of investigation	**Contributions of natural radionuclides to the total air kerma rate 1 meter above the ground level.**
	[nGy/h]
The first area- serie I	**94.15**
The first area-serie II	**119.69**
Reference area I	**33.78**
Stara Hałda	**58.83**
rejon "D"	**99.01**
Reference area II	**36.06**
Neutral territory	**36.04**

For the sites where it was applicable value of caesium’s contribution was estimated on base of relaxation mass [ICRP Report 53]. Results were presented in table 3.

Table 3. Caesium radiation’s contribution to the total air kerma rate

	Stara Hałda	**Reference area I**	**Reference are II**	**Neutral territory**

depth	ground density	Specific activity ^{137}Cs	ground density	Specific activity ^{137}Cs	ground density	Specific activity ^{137}Cs	ground density	Specific activity ^{137}Cs
[cm]	[g/cm^3]	[Bq/g]	[g/cm^3]	[Bq/g]	[g/cm^3]	[Bq/g]	[g/cm^3]	[Bq/g]
10	***0.56***	***0.101***	***1.09***	***0.026***	***0.81***	***0.068***	***1.08***	***0.1993***
50	***0.75***	***0.004***	***1.06***	***0.0055***	***1.09***	***0.0038***	***1.24***	***0.0475***
Relaxation mass [g/cm^2]	*16*		*32*		*18*		*36*	
Kerma rate [nGy/h]	**8.02**		**3.15**		**6.07**		**26.20**	

Due to the fact that all investigated sites lay on the similar height above the sea level the constituents from cosmic ray were assumed to be the same, 33.8 [nGy/h] [Lowder,W.M. & Miller, K.M.]. The impact of radionuclides dispatched in air could be estimated by calculation basing on results obtained during permanent control of air pollution that had been carried out for several years by station located in CMI, Katowice. Though the distance of about 50 kilometres from investigated sites, there was no evidence to the contrary. For calculation the highest observed concentration of beryllium was considered even though, the value was at the level of 10^{-4} [nGy/h]. A similar approach was applied in case of potential component of external radiation coming from radionuclides included in dust suspended in air. The derived concentration of radionuclides was about few Bq/m^3, so that the contribution to the total kerma rate was less than the kerma rate calculated in case of beryllium.

The behaviour of radon in investigated sites (as will have been pointed out in next paragraph) did not vary in comparison to common conditions, so that estimation of this constituent was carried out basing on result of measurement that had been done in Katowice. Again, the highest observed value of radon progeny concentration was taken into account. Even then, evaluated value of this kerma rate component was less than 7 [nGy/h] where the average was 1.2 [nGy/h].

The rates of all calculated components are shown in the figure 6.

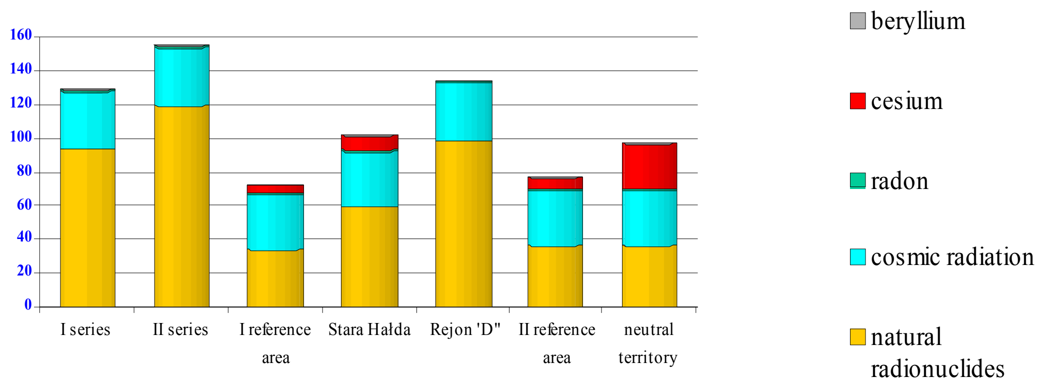

Fig. 6. Components of the air kerma free-on-air rate at 1 meter above the ground level [nGy/h]

Theoretically calculated values were compared with average measured values. The results are presented in figure 7.

Fig. 6. Comparison of average measured value of air kerma rate with values calculated basing on specific activity particular radionuclides [nGy/h]

Generally measured values conform theoretically to calculated ones. Only in two cases: second reference area and Stara Hałda, the differences are bigger than measurement uncertainty. This can be explained by attenuation of radiation by trees overgrowing these areas.

Taking into consideration all estimated constituents, there was a possibility to calculate impact of investigated spoil banks to potential risk at their surface excluding all local conditions. The net values of total air kerma rate on all investigated waste rock dumps are presented in figure 8.

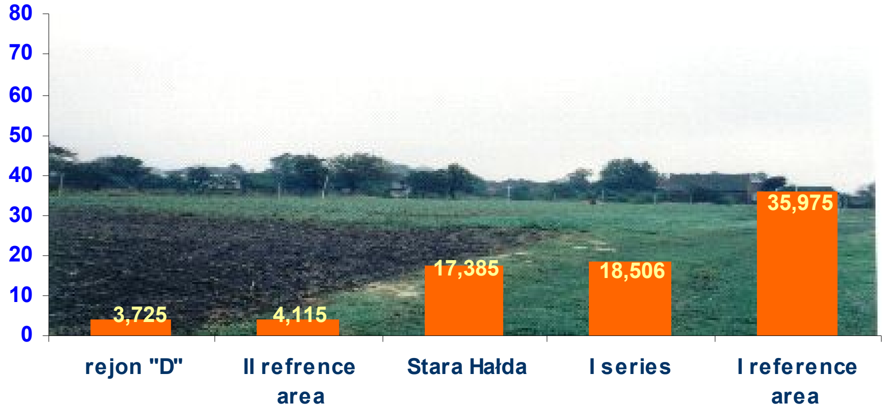

Fig. 8. Relative increase of air kerma rate on investigated spoil banks [nGy/h]

The biggest observed increment of air kerma rate on the waste rock dump in comparison to the relevant reference area was equal 76.25 [nGy/h] so that, making following assumptions:

- one-year time of exposure, 365 × 24 [h],
- risk concerned an adult person,
- the way of exposure was conform to the ROT (rotational geometry) model,
- average energy of gamma radiation was approximately equal 600 keV

and taking into account the reference values of conversion air kerma rate into effective dose factors [ICRU Report no. 57] the possible annual effective dose was as follow:

$$E = 0.814 * \Delta dK/dt = 0.542 \text{ mSv}$$

That constitutes about 20% of medium annual effective dose caused by natural radioactivity on the territory of Poland. But on the other hand, the calculated value is five times much more than the part derived from natural terrestrial outdoors radiation that is reported to be less than 0.1 mSv [Radiation Atlas of Poland, 1997],

Radon potential

The results of measurement of radon concentration in soil gas indicated that there was not clear relation between the radium concentration and occurrence of radon in soil. Even, bigger radon concentrations were observed in soil gas samples taken from reference area, as presented in figure 9.

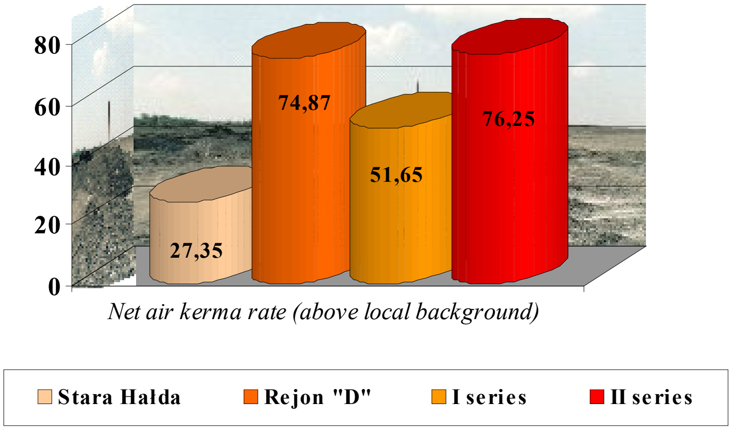

Fig. 9. Radon concentration in soil gas [kBq/m^3)

This result showed that in this case the influence of such properties of the ground as permeability or porosity is much more significant than the specific mass activity of radium. In spite of very wide range of radon concentration values observed, all of them were below the level 50 kBq/m^3, which is considered as high potential radon risk [Akerblom, 1986].

Natural isotopes in water

All results of radium concentration measurements were very low as shown in figure 10, close to the low limit of detection for the method applied for analysis. All result obtained were below maximum acceptable level for potable water of 0.1 [Bq/l]. The potential seasonal differences related to the amount of rainfall were not observed, too. Obtained results showed that even where was a certain impact of waste rock to radium concentration in permeating water, the final effect was not noticeable.

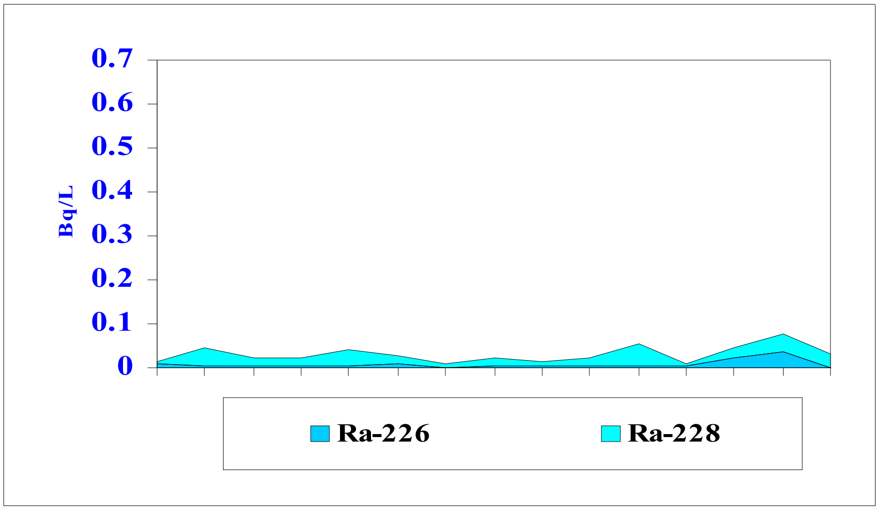

Fig. 10. Radium isotopes in surface water in vicinity of waste rock dump

Conclusion

Amongst all investigated agents of radiation risk only external radiation derived from slightly enhanced mass activity concentration of natural radionuclides was noticeable. Remaining ones such as radon and radon progeny and possible leaching of radionuclides to ground water did not differ at the significant level from their values that have been observed in the relevant reference areas. Calculated potential increment of effective dose should be taken into account during planing of developing of the sites where waste rock was or will have been used as landfill.

References

1. Akerblom G., Investigation on mapping of risk areas., Luela Sweden, Swedish Geol. Comp. Raport IRAP 86036. 15 pp., 1986.
2. Chalupnik S., Lebecka J., Determination of ^{226}Ra, ^{228}Ra and ^{224}Ra in water and aqueous solutions by liquid scintillation counting, Liquid Scintillation Conference, RADIOCARBON 1993, pp. 397-403.
3. ICRU Report 57, Conversion Coefficients for use in Radiological Protection against External Radiation , , 1998
4. ICRU Report No 53, Gamma ray Spectrometry in the Environment, 1994
5. Lebecka, J., K. Skubacz, S. Chałupnik, I. Tomza, I. Pluta, J. Skowronek Influence of mining activity on distribution of radium in the natural environment 1986 4th Working Meeting Isotopes in Nature, Leipzig, Proceedings, Part II, s. 423 - 428
6. Lebecka, J., S. Chałupnik, B. Michalik, M. Wysocka, K. Skubacz, A. Mielnikow Radioactivity of Mine Waters in Upper Silesian Coal Basin and its Influence on Natural Environment. 1994 5th International Mine Water Congress, Nottingham (U.K.)
7. Lowder, W.M., Miller, K.M. Cosmic and terrestrial gamma radiation measurement, , Fifth International Symposium on the Natural Radiation Environment, Commission of the EC, report EUR14411.
8. Michalik B., The inventory of mining setling ponds, GIG, 2002 (in Polish)
9. Michalik, B. , S. Chałupnik, J. Skowronek, J. Lebecka Guidlines for treatment of solid wastes with enhanced natural radioactivity in Polish coal industry 1995 Symposium on Radiation Protection Neighboring Counties in Central Europe, Slovenia, Portoroż 95, s. 145 – 149
10. Michalik, B. et al. - CONTAMINATION OF SETTLING PONDS OF COAL MINES CAUSED BY NATURAL RADIONUCLIDES, II International Symphosium on Technologically Enhanced Natural Radiation, September 1999, Rio de Janeiro, Brasil

11. Mielnikow,A., K. Skubacz, B. Michalik Quality assurance in natural radiation measurements. 1996 International Conference : Technologically Enhanced Natural Radiation Caused By Non - Uranium Mining, Poland
12. Radiologiczny Atlas Polski, Państwowa Inspekcja Ochrony Środowiska, Centralne Laboratorium Ochrony Radiologicznej, Państwowa Agencja Atomistyki, Biblioteka Monitoringu Środowiska, ISBN 83-85787-2-4, Warszawa 1998
13. Saldan M., - Biuletyn Instytutu Geologicznego, Warszawa, Poland, vol. 5, 1965 (in Polish).
14. Tomza I., Lebecka J., - Radium-bearing waters in coal mines: occurrence, methods of measurements and radiation hazard - Int. Conf. On Radiation Hazards in Mining, Golden, Co, 1981.
15. United Nations Scientific Committee on the Effects of Atomic Radiation, 1982 Ionising Radiation: Sources and Biological Effects. Report to the General Assembly, with annexes. UN sales publication E.82.IX.8. UN, New York, 1982.
16. Wysocka M., Lebecka J., Chałupnik S. – Environmental impact of radium-bearing waters from Polish coal mines – Int. Conference TENR I, Szczyrk 1996.

THE EFFECT OF EARTHQUAKE-INDUCED RADON RELEASE ON THE POPULATION IN THE SEISMIC ACTIVE REGIONS OF ARMENIA

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Abstract

For the first time on the basis of Spitak earthquake (December 1988 Armenia) experience it is found out that the earthquake causes intensive and prolonged radon splashes which, are contrastingly displayed in covered premises (dwelling houses, schools, kindergartens) even if they are at considerable distance from the epicenter of the earthquake. The interval of splashes includes the period starting from the first foreshock and ending by the last aftershock, i.e. several months. The radiation intensity and duration of the influence are in direct correlation with the force of earthquake. The area affected by radiation is larger than the territory of Armenia. The scales of this impact on the effected population is 12 times higher than the number of people injured in Spitak earthquake.

Keywords: radon, earthquake, Spitak, Armenia.

Introduction

Today actuality of radon problem is universally recognized. According to UAEA data it was established, that natural sources do the main contribution (to 70%) to the sum doze of irradiation (420 m bar a year). The main of them are considered materials with increased content of natural radionuclides, and radon is accumulated in buildings. About 44% of the sum doze of irradiation fall on radon and its radionuclides. Owing to this factor mortality is about 80 thousands people per year. Among principal consequences of radon irradiation the main consequence is cancer of upper respiratory tract and lungs, leukemia that happens with children, and etc. In many countries of the world (USA, Sweden, Great Britain) this problem was raised to the rank of rational and state programs.

Attention of foreign investigation is accented on radon harmfulness for those who inhabit unfavorable houses for a long period of time. Main sources of radon are considered building materials, mainly soils. According to IAEA data, localities with high content of radioactive elements in rocks are considered as “hot points” with increased content of radon. According to data of investigators of the former USSR, “radon storms”, which are caused by geomagnetic storms, effect human organism.

In geology the method of usage of radon radioactive emanation in soil waters and soil with the aim of seism prognosis, became worldwide famous after Tashkent earthquake in 1966 and after the discovery, made by Gorbushina and others.

Japanese investigators found small increase of radon concentration in the atmosphere during earthquakes (Spitak 1988).

There is no information in literature about the influence of seismic focus and the radius of its effects on radon concentration in lodgings. There are no data concerning estimation of dust radiation factor during destructions caused by earthquakes.

The suggested report is one of the first, in which to a definite degree the indicated deficiencies are taken into consideration.

Significantly dangerous are sites on which radon and radium concentrations are high in mineralized and ground waters respectively, oil-bearing basins and areas on which oil water precipitation tanks are located. Potentially harmful are known to be zones of the development of mountain rocks containing high concentrations of uranium, thorium, and radium as well as uranium deposits and ore occurrence areas. The latter being absolutely rightful for the stable state of the earth crust does not meet the requirements on radon threatened sites zoning in seismically active regions, where radon threatened are connected with the earthquake areas and active tectonic faults zones. Here, simultaneously with radioactivity of rocks, their physical-mechanical properties, textural-structural peculiarities that stipulate the percent of rock porosity, as well as such radiometric parameter as estimation coefficient – play a significant part. Moreover, soils display themselves in a not isolated way, but as a constituent of engineering-geological peculiarities of sites with all the ensuing consequences. Rather a significant factor is the extended character of radon emanation field occurrence; opinions concerning its formation differ. As a matter of fact, a contrast increase in radon concentration is a function of the earthquake.

The problem of human inhabitance surroundings in the general sphere of problems, connected with earthquakes, is usually considered only in one aspect – in the aspect of seism stable building and construction.

But, as the results of our especially ecological investigations have shown, catastrophic destructions provoked with earthquakes with all ensuing consequences, are only the visible part of iceberg.

It is possible to provoke an earthquake correctly, have seism stable houses, avoid direct human victims, yet it is impossible to avoid danger of death, if there is no knowledge about it.

This danger is radiation.

In this report we shall speak about α-radiation (radon radiation), on which we have a concrete factual material. It is necessary to mark, that, as the analysis of literary data has shown, other types of radiation conditioned by earthquakes, are not excluded.

However, as the results of our investigations have shown, the same houses at the same time of the year are characterized by different concentrations of radon at stable and extreme (earthquakes) condition of the Earth's crust.

Thus, on the example of the Spitak earthquake it has been determined, that earthquakes are accompanied by intensive and long-term α-splashes (radon splashes), local radiation fields of which are constantly manifested in closed lodgings (dwelling houses, schools, kindergartens) even on the considerable distance from the epicenter of the earthquake, thus repeatedly increasing the risk of α-radiation affection of the population.

These splashes are quickly cleared away in the open air, and that is why they are not usually registered.

Preliminary results of the work financed by Ministry of Education and Science of the Republic of Armenia started in 1989 by a small scientific collective to the department of geology and exploration techniques SEUA.

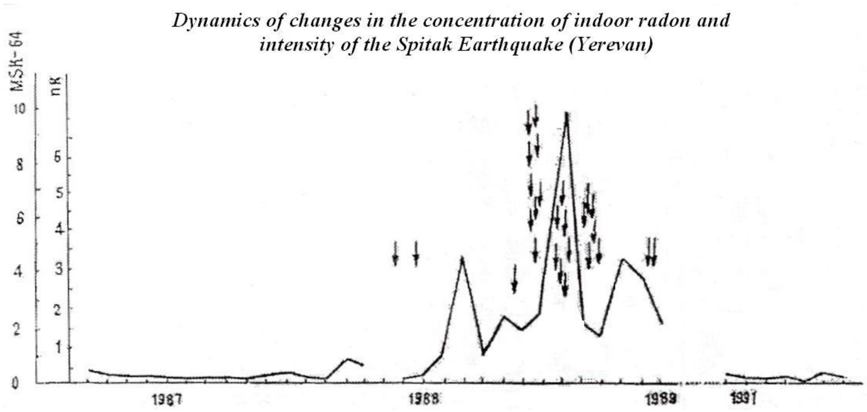
Subject and Methodology of Measurements

The research is underpinned by the results indoor radon monitoring conducted in Yerevan (Armenia) and its vicinities from 1987 to 1993 (stable and unstable situation of the Earth crust). The territory is formed by low radioactive volcanogenic sedimentary rocks. The Armenian is a highland region, characterized by young volcanism. The volcanic regions have not yet cooled and the region is seismically active. These active geotectonic processes and the increasing technology-induced on the environment make the public safety an issue of consideration for natural and technology catastrophes. Measurements were made applying a radon meter of FAS-P-2 model supplied with a filter of AFA-PSP-20 type manufactured in Russia. The instrument assures a 95% efficiency of radon aerosols catchments and measurement errors make some 40%. Air samples were taken in basements and measured in bases, single-and multi-stored buildings during the whole study period. While carrying out investigations, methodic recommendations were made up for measuring volume activity of radon and its daughter products in the air of dwelling houses and settlements in Armenia. One of develops of the recommendations is the co-author of this article.

Total amount of taken and analyzed samples is 5228. Mean monthly values of measurements are generalized irrespective of the type of buildings through a moving average formula, and graphs have been constructed based on data obtained.

Results and discussion

Statistical processing of data of radon monitoring results (fig.1), graphically brought into coincidence with dynamics of the earthquake, showed clearly that, irrespective of season oscillations, radon concentration in lodgings for the space of the whole 1987 year was much lower of the sanitary norm of 4 πkm/per, not exceeding on the whole 5 πkm/per during the whole year.



Dynamics of changes in the concentration of indoor radon and intensity of the Spitak Earthquake (Yerevan)

(fig.1)

The tendency to growth is marked from the beginning of the year 1988, exceeding radon concentration in July-August, according to measurements of the same time in 1987, nearly 8-10 times. In separate months (in January, 1989) the middle level of radon concentration was increased nearly 14 times.

As it may seen from the graph, three spikes are notable, which characterize intensive splashes of radon, corresponding, with some delay in time, to the first foreshock, to the main shock, and to late after shocks.

This allows to determine clearly time intervals, which are characterized by multiple increase of radon concentration in closed lodgings – from the first foreshock to the last aftershocks.

It is interesting to note, that on the whole the spike of radon in houses of Yerevan, conditioned by the shock, is as if a delayed in timer mirror reflection of the graph of subsoil radon monitoring, registered at Gyumri regime station by V.P. Rudakov and Basnetsian (fig.2); they differ only in the change of concentration levels.

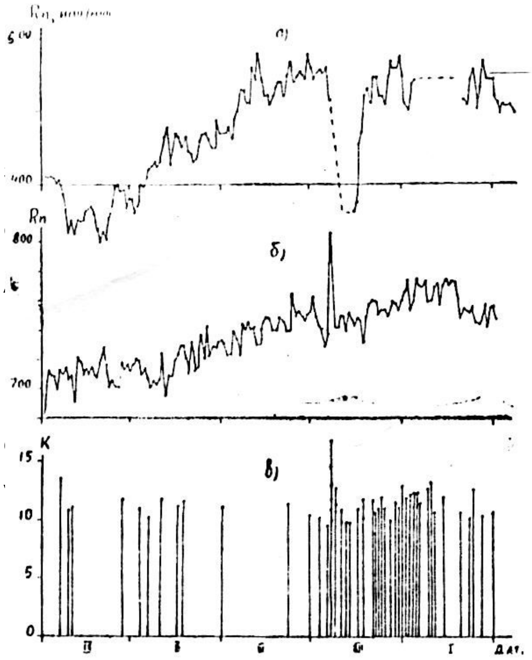


Fig 2. Spitak Earthquake operational Precursors:

a) Leninakan seismic station b) Jermuk seismic station c) Seismic activity in the region

investigator can determine by intersection only
aracterized by the increase or decrease of
l background.
the question is not only about the repeated
before the earthquake, but also about the
n of radon variations dynamics indoor radon,
e Earth's crust.
tions of the room-radon in the city Yerevan in
indices of the variations are given bellow:

Year	Mean concentration	Dispersion α^2	Root mean square dispersion, d	Variation coefficient V%
1987	0.25	0.0106	0.0103	41.32
1988	1.126	0.864	0.924	82.5
1989	2.977	4.444	2.109	70.81
1991	0.17	0.004	0.069	37.05

They indicate their essential distinctions at stable (1987,1991) and tense (1988,1991) condition of the Earth's crust.

At the same time, as it may be seen from the fig.1,2, by its contour it co insides with the positive spike at Jermuk regime station. Given data allow to speak about the splash into the atmosphere in the epicenter part and about its intensive accumulation in the subsoil layer on the considerable distance from it.

It is important to note that actually there is no vivid central spike, and, according to data of every day measurements, this whole interval before and after the earthquake is characterized by dozens of spikes, as it follows from the fragments of the graph of every day measurements (fig.3).

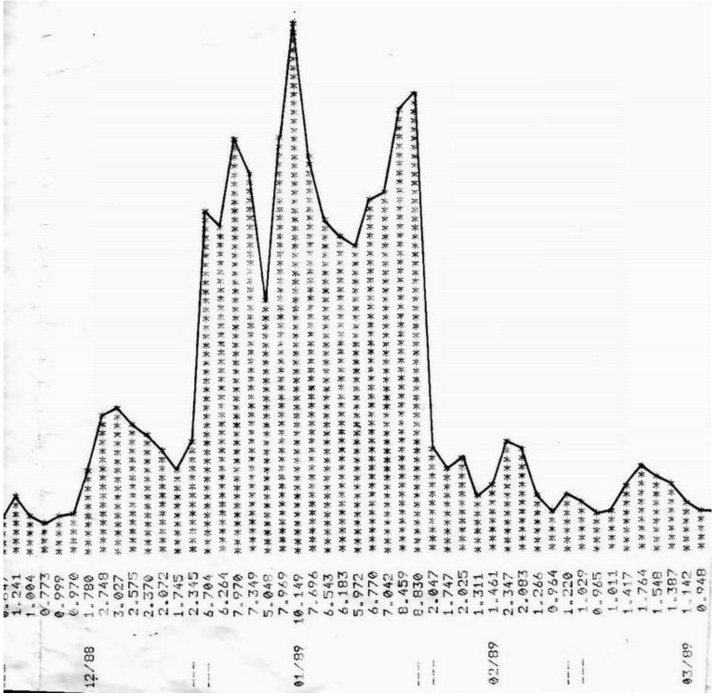


Fig 3. Fragments of the graph of everyday measurements.

The graph of calculations of equivalent irradiance doze is given in (fig.4). As it may be seen from the graph, here also the curves characteristic for stable state and for the state during the earthquake, are distinctly seen enough. In doing so, if for the 1987, 1991, 1992, and 1993 years abruptly lowered equivalent irradiance dozes from 0,183 to 0,435 mzv are characteristic, i.e. less than twice in comparison with the average global magnitude, then in January, 1989, the effective equivalent irradiance doze at the expense of radon and its radio nuclides was about 16 mzv, i.e. 50 times more than the mean equivalent radiation doze by radon of the above-mentioned years and 16 times more than generally-accepted mean quantity by radon.

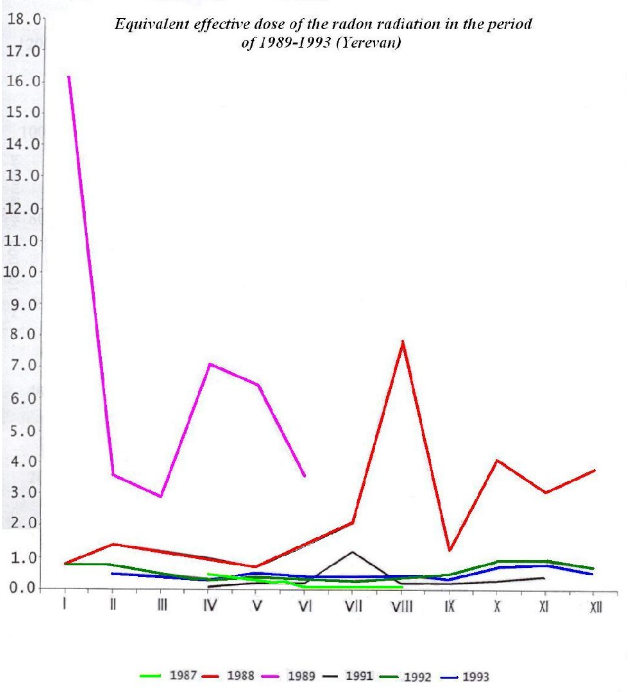


Fig. 4

In the epicenter part of the earthquake hearth (Nalband, Spitak and alongside the whole disaster zone), the level of radiation background of dwelling houses as well as the effective radiation doze by radon was many times higher.

The following facts which have not received explanation till now can be considered as consequence of long-lasting radiation influence on human organism: long-lasting state of apathy and indifference typical for the population of Armenia during the period of more than a year after the earthquake, prevalence of respiratory diseases and digestive system diseases (fig.5), prevalence of malignant cancer forms in disaster zones and the lungs cancer over the other forms of oncology diseases (fig.6, 7), prevalence of mental disorders of the children’s (fig. 8), etc. (Source: Ministry of Health of Republic of Armenia, Statistical data on public health.)

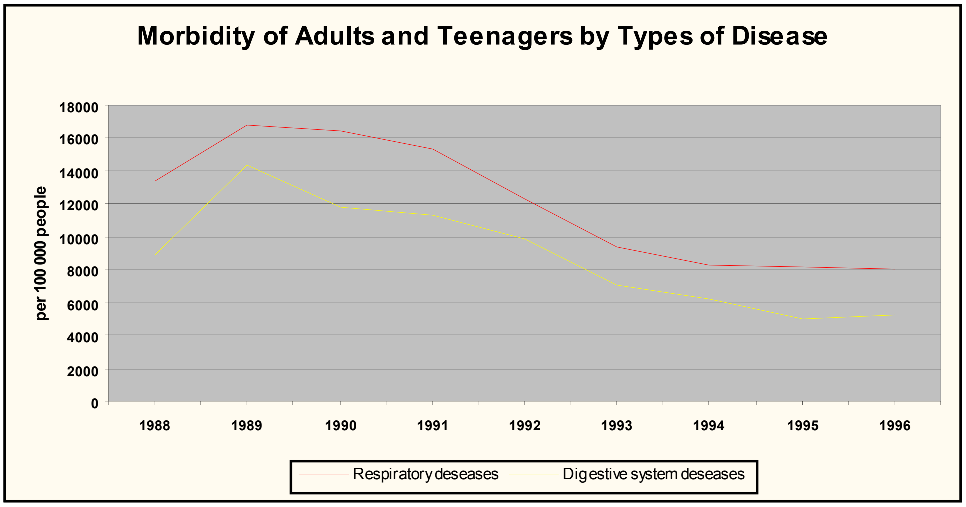

Morbidity of Adults and Teenagers by Types of Disease
per 100 000 people
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
1988
1989
1990
1991
1992
1993
1994
1995
1996
Respiratory deseases
Digestive system deseases

Fig 5.

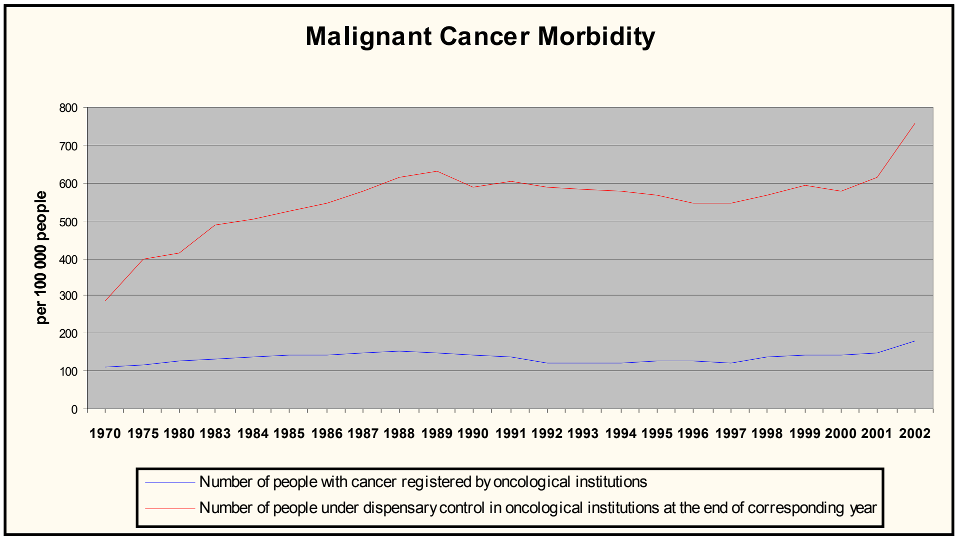

Malignant Cancer Morbidity
per 100 000 people
800
700
600
500
400
300
200
100
0
1970 1975 1980 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002
Number of people with cancer registered by oncological institutions
Number of people under dispensary control in oncological institutions at the end of corresponding year

Fig 6.

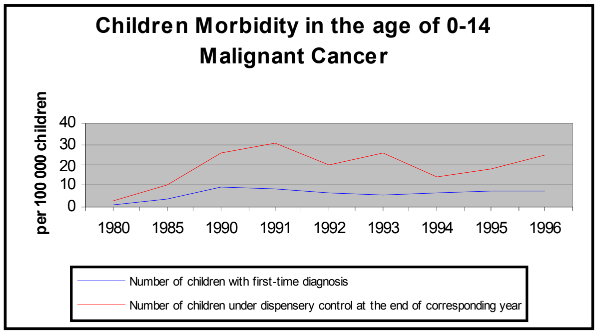


Fig 7.

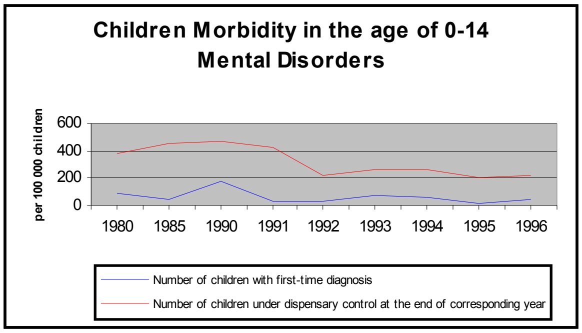


Fig 8.

The area affected by radiation is larger than the territory of Armenia. The scales of this impact on the affected population is 12 times higher than the number of people injured in Spitak, Leninakan, and other settlements (toll of injured – 25 000 people, compared to the projected diseases caused high level of radiation in no adapted population – over 300 000).

The obtained results give the opportunity to introduce definite correctives into the existing notions about natural ionizing sources and their exciters, and all the epicenters of earthquakes with the radii of their influence in seism active regions to consider as “hot points’ of our planet in connection with radon.

At the same time a series of questions, connected with the radiation problem conditioned by earthquakes, are to be solved and affirmed on the example of other seism active regions, and they demand joint efforts of investigators of different countries.

The author of this report has developed a program of investigations in this sphere, which may be discussed with those who are interested in the problem.

It is quite evident, that side by side with existing aspects of investigations, connected with earthquakes, it is necessary to develop a new aspect: earthquake and ecology of man. This aspect should be aimed at the study of phenomena, conditioned by earthquakes and influencing man (radiation, ionized air, electromagnetic field, ultrasound, and etc.).

Conclusions

As a result of performed works the following preliminary conclusions were received:

- In seism active regions with tense conditions of the earth crust a paramount role, as a radon source, acquire not simply soils themselves, but also soils as a component of engineering-and-geological peculiarities of territories which have been built and territories which are in the process of building. The important role, for all that, play both the composition and physical-and-mechanical peculiarities of soils and the level of soil waters, availability of small breaks and zones of micro penetrability. All this, as a whole, predetermines the intensity of radon exhalation in the air of lodgings.
- Radon in the air of closed lodgings and at home not only accumulate there, but also change contrastingly its composition on the eve of the earthquake. That is why monitoring of the room radon may be used as a part in the system of seism prognosis methods.
- Contrast increase of radon concentration in places fit to live is characterized by long keeping of its high concentration also after the earthquake before stabilization of tense seism active condition of the territory. This fact increases many times the degree of risk of α-radiation (radon) effect on the population

and permits to consider radon not only as an indicator, but also as a promoter of cancer diseases.

The danger of the influence of natural radiation provoked by the earthquake exists for all urban territories of seism active regions, and it requires coordination of investigation in different countries according to precisely elaborated programs.

Among the problems of Disaster Medicine a new problem – radiation safety of the population in earthquakes – should be distinguished.

Literature

1. Balasanyan S., Cisternas A., Melkumyan M. Earthquake Hazard and Seismic Risk Reduction, London, 2000, 448p.
2. Bolt B.A. etc. Earthquakes. San Francisco, 1978, 241p.
3. Krisiuk E.M., Parkhomenko V.I. Radiation background of residential buildings. Atom energy, vol. 57, pp. 43-48.
4. Nazarov V.F., Nero A.V. Radon and its decay products in indoor air. New-York, Singapur 1998.
5. Petrosyan A.A., Gasparyan A.G., Krisiuk E.M. – Survey/measurement of velum activity of radon and its derivatives in the air of living quarters and inhabited areas. Arm SSR, 1990.
6. Rikitake T. Earthquake Prediction. Elsevier Scientific Publishing. Co Amsterdam, 1976, 357p.
7. Sagatelyan E.A., Petrosyan A.A. - Seism active zones/territories of advanced radiation hazard. International Congress Women for Environmental Protection. Moscow 1993.
8. Sagatelyan E.A., Petrosyan A.A. etc – Risk of α-radiation of affections of population during the earthquakes. Inter. Conference of earthquakes, Yerevan 1993.

9. Sagatelyan E.A. and others – Room radon monitoring in the system of Seism prognosis methods. Inter. Conference of earthquakes, Yrevan 1993.
10. Sagatelyan E.A., Petrosyan A.A. - Character and danger of radiation by Earthquake 1988 Spitak. Armenia international seminar, Main issues of Disasters medicine and importance of Moral-physiological factor in major disasters, p.164, Yerevan 1997.
11. Sagatelyan E.A., Sagatelyan Art.K., Radioecological properties of natural construction materials. Collection of annual scientific conference materials of SEUA, vol. 2, Yerevan 2000, p. 401.
12. Sagatelyan E.A., Population radioecological safety at earthquakes. International seminar. Armenia conversion potential and ISTC programs. Abstracts, Yerevan 2000, p. 191.
13. Sagatelyan E.A., Petrosyan A.A., Matevosyan E.K., Risk of α-radiation of affections the earthquakes. Conference of earthquakes, Yerevan 1997.
14. Sagatelyan E.A. On radio ecological studies in Armenia. Int. Union of Radioecol. 36, 2000, p.15-16.
15. Shemyi-Zadeh A.E. Radon and solar activity. Environment, 1992, pp. 31-35.
16. Character and danger of radiation by Earthquake 1988 Spitak. Armenia international seminar Main issues of disasters medicine and importance of Moral-physiological factor in major disasters, p.164, Yerevan 1997.
17. Live in radiation. NRNB, 1998.
18. Radiation, dosages, effect, risks. Moscow, 1990, pp. 22-31.
19. Some aspects of radon eco-geochemistry of seism active regions. International symposium on applied geochemistry. CIS countries, p. 206, Moscow 1997.

RADIUM IN GROUND WATER CLOSE TO BUENA LAGOON IN COASTAL ZONE OF RIO DE JANEIRO STATE, BRAZIL

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Abstract.

Ground water close to the head of Buena Lagoon has high salinity and low pH values. Radium is present predominantly as ^{228}Ra. Factors responsible for high radium mobility in ground water seem to be high salinity with resulting competition for adsorption sites, and low pH values with resulting limited adsorption of Ra^{2+} on positively charged surface of adsorbents. Behavior of uranium and thorium is also influenced by their speciation and low pH conditions. Uranium is present as positively charged uranyl ion UO_2^{2+} in low pH samples and is very mobile. Similarly, presence of

positively charged Th^{4+} and thorium complexes with sulfate result in relatively high thorium concentrations at low pH range. On the other hand, mobility of phosphate released from dissolving monazite is probably reduced due to its adsorption and precipitation close to its source.

Keywords Groundwater, Coastal aquifer, Water geochemistry, Natural radioactive isotopes, Rio de Janeiro.

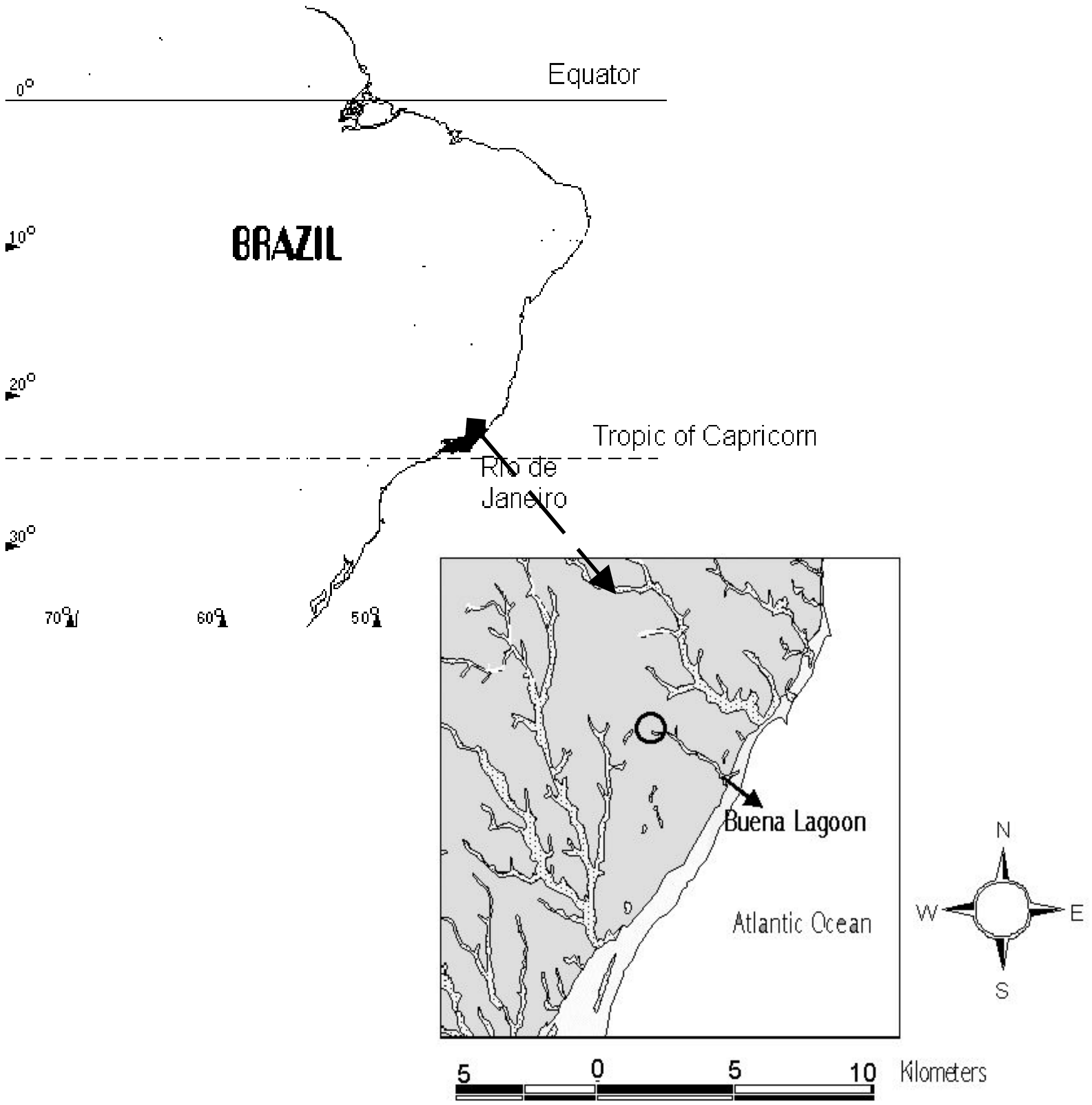
Introduction

Several natural radioactive elements are present in ground water and surface water at coastal zone close to Buena Lagoon in Brazil, but only the long-lived radium isotopes ^{226}Ra and ^{228}Ra are found in concentrations that are significant from the point of view of potential effect to human health (Lauria and Godoy 2002; Almeida and others in press). The behavior of radium and actinide elements in environment is of interest not only from the point of view of their environmental impact, but also because the environmental behavior of radium can be considered analogous to the behavior of ^{90}Sr, and the thorium behavior is considered to be similar to the behavior of ^{239}Pu (Krauskopf 1986). Both radionuclides are present in nuclear wastes.

Behavior of radium in environment is controlled by adsorption and co-precipitation. In fresh water system, radium tends to be rapidly adsorbed from aqueous phase, and its mobility is quite limited. Among water chemical parameters, increased salinity and/or low pH have been observed as important parameters responsible for high dissolved radium concentration (Kraemer and Reid 1984; Lauria and Godoy 2002). Of its aqueous species, Ra^{2+} is likely the most important in the environment, but complexes like $RaOH^+$, $RaCl^+$, $RaCO_3^0$ and $RaSO_4^0$ may influence radium mobility in water (Beneš and others 1982; Beneš 1984; Langmuir 1985). Behavior of uranium depends on redox conditions. Dominant forms are U(VI) under oxidizing conditions and U(IV) under reducing conditions. Concentrations of U(IV) are quite low because they are controlled by precipitation of low solubility minerals such as UO_2(am). In contrast, U (VI) may be present in high concentrations as positively charged uranyl ion UO_2^{2+}

under low pH conditions and becomes increasingly adsorbed when pH increases. At neutral and alkaline pH range, carbonate complexes such as $(UO_2)_2(CO_3)_2^{2-}$ predominate and dissolved uranium concentrations become high again. Thorium is present only as Th(IV) and solubility of Th minerals like ThO_2 is low. Adsorption of Th^{4+} becomes more important with increasing pH values. There is formation of complexes such as $Th(HPO_4)_3^{2-}$, $Th(SO_4)_2^0$, and $Th(OH)_4^0$ (Langmuir and Herman 1980), and some thorium complexes like $Th(OH)_4^0$ have high affinity for adsorption.

Fig. 1 Buena Lagoon localization



In waters of the Buena Lagoon in the north of Rio de Janeiro state-Brazil (Fig. 1), in a region rich in monazite, high concentrations of dissolved ^{226}Ra and ^{228}Ra have been found. These findings resulted in a survey aiming to investigate the origin of high observed radium concentrations. During this investigation, several springs with high concentrations of radium have been discovered close to the Buena Lagoon (Lauria and others 2002). The objectives of this paper are characterization of ground water and spring water, identification of causes of high concentrations of radium and other radionuclides in water, and contribution to better understanding of behavior of radium and other radionuclides in coastal tropical environment.

Materials and methods

There was sampling of waters from 4 springs (S) 3 private wells (PW), and 6 new wells (W) located close to the Buena Lagoon head. Additionally, there was sampling of solid phase from the boreholes surrounding the springs. Geographical location of the sampling points was determined by a satellite navigation system, GPS (Garmin, model 45 XL). The sampling point locations are shown in Fig. 2

Approximately 3 liters of sample were collected. The physical-chemical parameters (pH, Eh, temperature, and electrical conductivity) were measured in the field. Alkalinity was determined in the field by titration with H2SO4. For thorium, uranium, earth rare element, major cation, metal and radium isotope determinations 2 liters of each sample were filtered by a Millipore membrane (0.45 μm), and samples were acidified with ultra pure HNO3.

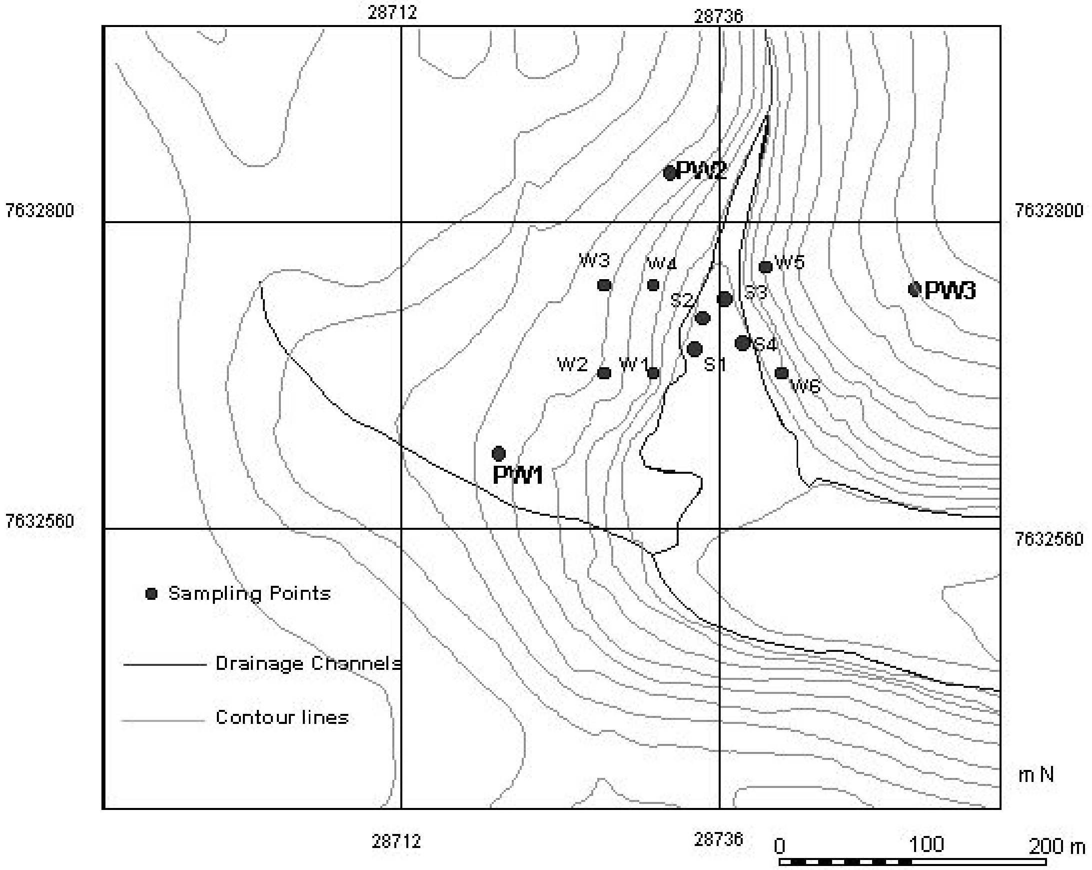


Fig. 2 Location of sampling points: springs (S), private wells (PW), and drilled wells (W) at the head of the Buena Lagoon.

Alpha and beta total counting, in a proportional counter of small area performed determinations of the activities of ^{226}Ra and ^{228}Ra in water. Radium was concentrated by co-precipitation with $BaSO_4$. To one liter of sample was added H_2SO_4 and $BaCl_2$ and $Ba(Ra)SO_4$ was co-precipitated. The sulfate was washed and dissolved with nitrilotriacetic acid (NTA). Barium (radium) sulfate was re-precipitated by adding acetic acid until pH 4.5-5.0. The aqueous and solid phase were separated and the $Ba(Ra)SO_4$ was purified by dissolution in an ethylene diamine tetra-acetic acid (EDTA) solution at pH 10. Then the sulfate mixture was re-precipitated by acetic acid (pH 4.5-5.0). The precipitate was filtrated and after one month of growth, ^{226}Ra was determined by gross alpha counting. ^{228}Ra was determined by beta counting, whereas the alpha particles of ^{226}Ra were stopped by a filter paper. Corrections were made if there was any contribution from the daughter products of ^{226}Ra. Alpha and beta activities were counted in a low-background anticoincidence proportional detector (Bertold, model: LB770-1) (Godoy and others 1994).

Th, U, light earth rare elements (La-Sm), major cations Ca, Mg, Na, K, and metals Mn, Al and Fe were determined by by inductively coupled plasma-mass spectrometry, ICP-MS, Perkin-Elmer SCIEX ELAN 6000, after a dilution 1:20 with water quality Milli-Q, applying so-called TotalQuant® method and In and Tl internal standards (Lauria and Godoy 2002).

About 0.5 L of the sample was filtered through Millipore membrane (0.45 μm) for the determination of chloride (Volhard's argentometric method), sulfate (turbidimetry) and fluorine (by selective electrode). Approximately 0.25 L of the sample was filtered by glass fiber filter, and stored in dark glass flasks. These samples were analyzed for nitrate spectrophotometrically after its reduction to nitrite in a cadmium/copper column and for phosphate by the ammonium molybdate/ascorbic acid method (Standard Methods 1975).

Soil samples were collected from the soil-water interface in the bore well bottoms (1.5 to 3.3 m depth). The soils were transferred to plastic bags and pH and Eh measurements were immediately performed. At the laboratory the samples were air dried and passed through a 2 mm sieve. Then, around 300 g of sample were transferred to a polyethylene bottle and after 20 days, the samples were analyzed by gamma spectrometry for ^{226}Ra (^{214}Pb 614 keV) and ^{228}Ra (^{228}Ac 911 keV) determinations (Carnet and Jacquemin 1990). The other soil analysis were performed in the National Soil Research Centre-CNPS (Embrapa): particle-size by pipette method, cation exchange capacity (CEC) by ammonium acetate and potassium chloride methods, iron oxides by sulfuric acid extraction and titration with EDTA and organic carbon by reduction of dichromate by organic matter (Embrapa, 1997).

Results and Discussion

General hydrogeochemistry

The results of water analyses are presented in Tables 1, 2, and 3. Presumed ground water flow direction follows topographic gradient, e.g., it is from slopes towards springs S1-S4 in flat swampy area close to the Buena Lagoon head (Fig. 2). Thus, the swamp close to the Buena Lagoon head is discharge zone for ground water recharged on surrounding slopes.

Table 1 Earth rare elements, thorium, and uranium concentrations, and radium isotope activities in ground water samples collected close to the head of Buena Lagoon

SITE	**La** µg/L	***Ce*** µg/L	**Pr** µg/L	**Nd** µg/L	**Sm** µg/L	**Th** µg/L	**U** µg/L	**^{226}Ra** Bq/L	**^{228}Ra** Bq/L
S1	51.61	115.40	15.25	59.03	11.48	0.22	3.72	0.43	1.81
S2	52.33	118.60	16.23	67.66	12.36	0.15	2.79	0.49	1.68
S3	52.65	118.50	15.09	62.48	10.36	0.09	2.44	0.52	2.18
S4	45.70	101.60	13.00	52.73	9.72	0.22	1.79	0.53	2.50
PW 1	30.74	66.49	8.20	29.36	5.26	0.05	0.73	0.58	3.17
PW 2	8.67	14.75	1.72	7.07	1.13	0.05	<0.01	0.56	1.83
PW 3	0.12	0.27	0.03	0.41	0.16	<0.04	0.07	0.17	0.38
W1	6.96	13.01	1.46	6.46	1.31	0.13	0.26	0.11	<0.05
W2	29.14	54.42	6.52	23.99	3.92	0.25	0.78	0.27	1.87
W3	0.88	1.43	0.18	0.95	0.24	0.02	<0.01	0.01	2.00
W4	27.42	48.18	5.40	19.58	2.97	0.03	0.17	0.37	1.43
W5	3.12	11.10	0.92	3.22	0.57	0.25	0.17	0.01	0.01
W6	45.01	98.01	8.57	29.37	4.56	0.08	0.38	0.35	0.97

Ground water is of Na-Cl type, with elevated concentrations of sulfate in some samples. This is consistent with expected strong impact of marine aerosols on ground water chemistry in coastal zone. Only few samples with pH values > 5.5 exhibited significant values of alkalinity. Most samples had much lower alkalinity values, less than 2 mg/L as HCO_3^-. In all samples, the concentrations of phosphate were less than detection limit of 0.03 mg/L. The values of redox potential Eh_{H2} were very positive (from 315 to 582 mV). Concentrations of F^- were significant in some samples (S1, W4, and W6). They may be related to the dissolution of minerals like apatite caused by generally low dissolved calcium concentrations. Low pH values were observed at other regions of coastal zone of Rio de Janeiro state (Almeida et al., in press) and they are probably related to several factors, including evaporation and lack of carbonate buffers in soil.

Table 2 Major cation and metal concentrations in ground water samples collected close to the head of Buena Lagoon

SITE	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Al mg/L	Si mg/L	Mn mg/L	Fe mg/L
S1	564	64.18	22	10.8	4.76	2.25	0.06	0.26
S 2	229	71.36	23	12.7	5.47	2.38	0.08	0.24
S 3	240	71.19	23	13.3	5.28	2.48	0.09	0.38
S 4	400	74.65	25	13.0	4.85	2.47	0.08	0.23
PW1	528	60.50	19	11.6	3.16	1.92	0.06	0.31
PW2	456	33.91	28	15.9	0.26	0.50	0.04	0.10
PW3	501	39.43	24	9.6	0.06	1.55	0.03	0.13
W1	305	36.12	11	14.0	0.38	1.36	0.04	0.21
W2	567	76.65	29	43.8	0.03	1.79	0.08	1.30
W3	337	42.94	23	23.6	0.09	1.41	0.07	0.16
W4	527	66.16	23	38.0	1.48	2.59	0.20	1.92
W5	441	56.20	23	34.1	0.05	1.69	0.28	0.44
W6	528	61.78	26	24.6	1.23	2.81	0.18	1.44

Table 3 Major anion concentrations, pH, and electrical conductivity values in ground water samples collected close to the head of Buena Lagoon

SITE	**Nitrate** mg/L	**Sulfate** mg/L	**Cl** mg/L	**Alkalinity** mg/L HCO_3	**F** mg/L	**pH**	**Eh_{H2}** mV	**Cond.** $mS.cm^{-1}$
S 1	3.14	78.26	962	<2	0.23	3.70	496	4.01
S 2	1.09	20.43	327	<2	0.11	3.70	517	4.37
S 3	0.79	32.95	416	<2	0.11	3.74	447	4.53
S 4	2.17	7.13	655	<2	0.10	3.80	415	4.16
PW1	5.99	6.26	744	<2	<0.01	3.78	468	4.11
PW2	4.26	7.65	466	<2	0.09	4.66	513	2.24
PW3	7.06	5.47	337	916	0.04	6.79	492	1.70
W1	3.13	66.95	476	<2	0.08	4.60	462	2.05
W2	23.2	85.21	903	405	0.02	5.86	607	3.94
W3	10.22	70.43	536	208	0.02	5.63	569	2.24
W4	0.91	91.30	883	<2	0.20	4.39	406	3.59
W5	0.07	121.73	734	173	0.05	5.86	315	3.04
W6	0.18	99.13	734	<2	0.32	4.59	367	3.27

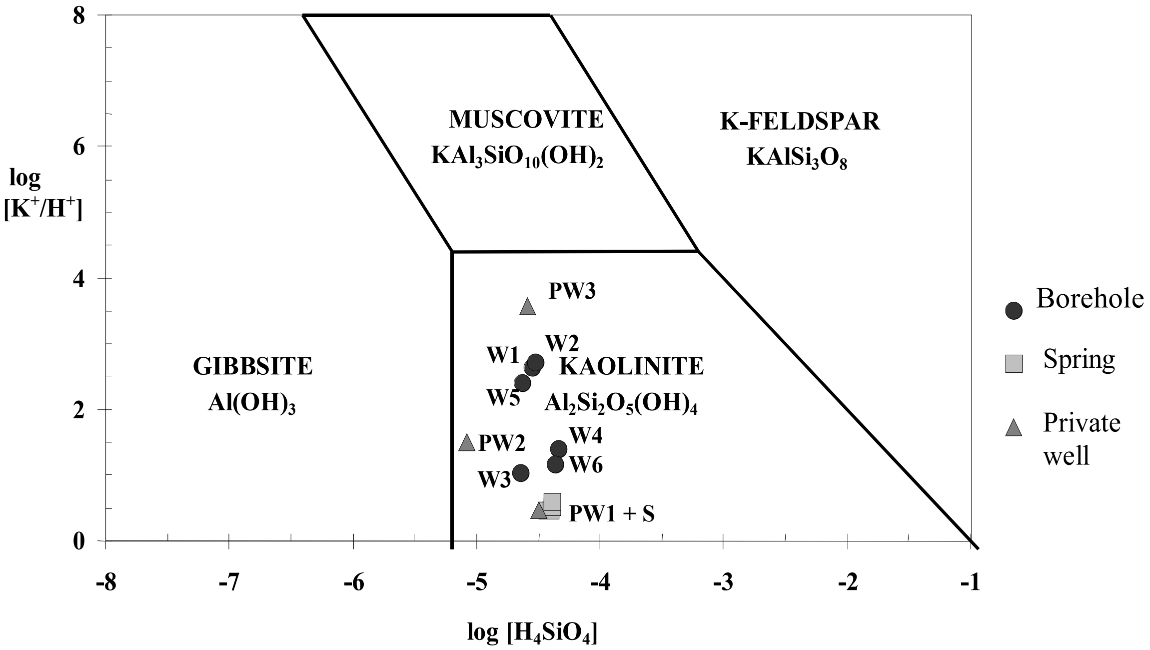
Saturation indices (SI) for selected minerals calculated with program PHREEQC (Parkhurst 1995) are in Table 5. All samples were undersaturated with respect to gypsum, and amorphous silica, and most samples were undersaturated with respect to amorphous $Fe(OH)_3(a)$. In contrast, all samples were supersaturated with respect to goethite, which is more stable mineral of ferric iron in aged sediments. All samples were undersaturated with respect to $Al(OH)_3(a)$ and samples with pH > 4.5 were supersaturated with respect to gibbsite. Samples generally were close to equilibrium with kaolinite (SI values not shown), which is consistent with the presence of minerals of kaolinite group like nacrite in soil (see solid phase discussion).

Table 4 SI values for selected minerals

Sample/mineral	$Fe(OH)_3$(a)	Goethite	$Al(OH)_3$ (a)	Gibbsite	Gypsum	SiO_2(a)
S1	-3.94	**1.95**	-4.14	-1.45	-2.75	-1.71
S2	-3.90	**1.99**	-3.83	-1.26	-3.20	-1.69
S3	-3.59	**2.30**	-2.98	-1.13	-2.98	-1.67
S4	-5.18	**0.70**	-3.81	-1.10	-3.71	-1.67
PW1	-3.59	**2.30**	-3.89	-1.25	-3.80	-1.78
PW2	-1.45	**4.44**	-3.47	**0.25**	-3.47	-2.36
PW3	**1.65**	**7.54**	-3.83	**1.98**	-3.83	-1.87
W1	-1.98	**3.89**	-2.71	**0.00**	-3.03	-1.91
W2	**1.95**	**7.85**	-1.18	**1.53**	-2.64	-1.79
W3	**0.86**	**6.73**	-0.97	**1.73**	-3.84	-1.90
W4	-2.66	**3.22**	-2.75	-0.05	-2.62	-1.63
W5	-0.48	**5.39**	-1.06	**1.65**	-2.51	-1.82
W6	-3.15	**2.73**	-6.26	-3.55	-3.83	-1.59

Bold: supersaturation

Fig. 3 Stability diagram for a K_2O-Al_2O_3-SiO_2-H_2O system with ground water samples



Concentrations of dissolved aluminum were relatively high as a consequence of low pH values. Stability diagram for a K_2O-Al_2O_3-SiO_2-H_2O system is in Fig. 3. There is a scatter of points in kaolinite field, suggesting formation of kaolinite at well drained sites. At some sites, there may be transformation of kaolinite to gibbsite as suggested by a point close to the gibbsite field. However, gibbsite becomes unstable at pH values about 4.2 (Appelo and Postma 1993; Langmuir 1997) and releases dissolved aluminum. There were increased sulfate concentrations in some samples from drilled wells and springs (1-3), but dissolution of gypsum can be excluded because concentrations of dissolved calcium are low. Thus, the most probable sources of sulfate are marine aerosols and oxidation of pyrite.

Behavior of radionuclides

Speciation of uranium, thorium and radium.

Concentrations of uranium were in the range from less than 0.01 to 3.72 μg/L (Table 1). High Eh_{H2} values suggest that uranium is present predominantly as U (VI). Thorium concentrations were in the range from 0.02 to 0.25 μg/L. Activities of ^{226}Ra were in the range from 0.01 to 0.58 Bq/L and activities of ^{228}Ra were in the range from <0.05 to 3.17 Bq/L. The highest radium activities were found in ground water from PW1.

Hydrogeochemical speciation of radionuclides was performed using PHREEQC program (Parkhurst 1995) and data from llnl (Lawrence Livermore National Laboratories) database implemented in PHREEQC-2 (Parkhurst and Appelo 1999). Equilibrium constants for radium were taken from Langmuir and Riese (1985). Total uranium concentrations were split on the basis of field Eh_{H2} values.

Results of radium speciation indicate that in all samples the predominant species of radium is free ion Ra^{2+}. Role of $RaSO_4^0$ complex is not significant even in samples with relatively high sulfate concentration (Samples S1 and W5) The complex comprises about 3 % of total radium in sample S1 and about 5 % in sample W5 with high sulfate concentration and low concentration of dissolved radium.

Thorium is present in low pH samples mostly as Th^{4+} or forms complexes with sulfate and fluorine. Complex $Th(SO_4)_2$ plays an important role in samples with high sulfate concentration (39 % of total thorium in sample S1). Other important complexes are $Th(OH)_2^{2+}$ and ThF_3^{+}. In samples with high pH values, complex Th $(OH)_4^0$ comprises most of dissolved thorium (97 and 95 % in samples W2 and W3, respectively) and other complexes are relatively insignificant.

Uranium is present as positively charged uranyl ion, UO_2^{2+}, in samples with low pH values (93 % of total U(VI) in sample S1). However, complexation with sulfate, chloride, and fluorine also plays a significant role. Complexes with carbonates such as $UO_2CO_3^0$ and $UO_2(CO_3)_2^{2-}$ are important only in samples with relatively high pH and alkalinity (56 % and 43 % in sample W3, respectively).

The light earth rare elements are predominantly in the form of free ion (La^{3+} and Ce^{3+}). In sample PW3 with the highest pH value (6.79), besides the free ionic species (~70%), the LREEs form complexes with carbonates.

Solid phase composition and adsorption of radium

Solid phase data based on samples collected from the bottom of boreholes are in Table 5. Relatively complete analyses are available only for boreholes W3 and W4. Soils have a significant fraction of clay, reaching values of about 40 %. Values of CEC are between 2.6 and 9.7 meq/100 g. Organic matter content is low, less than 1.0 wt %. Thus, contribution of organic matter to adsorption is negligible. On the other hand, concentrations of Fe(III) expressed as goethite are higher, between 1.3 and 2.57 wt %. Thus, ferric oxides and hydroxides probably play a significant role in adsorption of radionuclides. Value of pH_{ZPC} for goethite is about 7.3, and this means that surface charge is positive at the observed pH range surface (Langmuir 1997; Drever 1997).

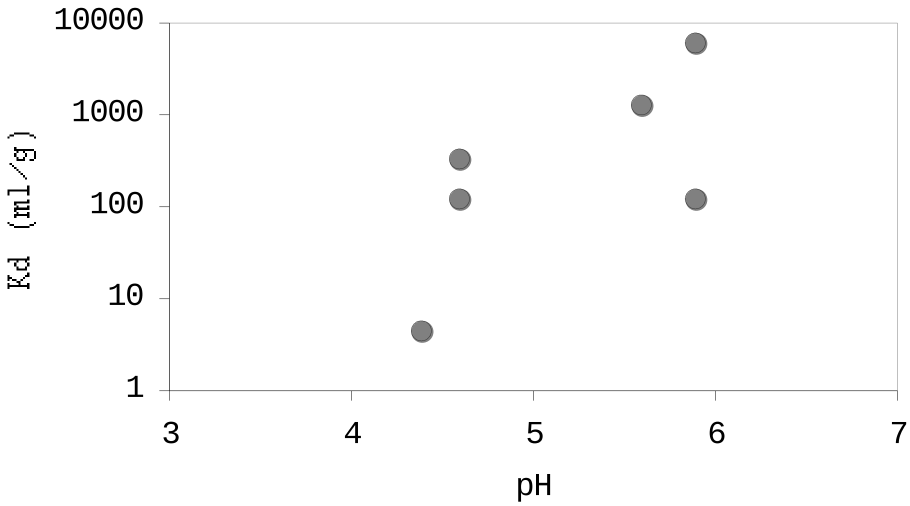
Table 5 Solid phase data

Site	$^{226}Ra_w$ [Bq/L]	$^{228}Ra_w$ [Bq/L]	$^{226}Ra_s$ [Bq/kg]	$^{228}Ra_s$ [Bq/kg]	K_d [L/kg]	Clay [%]	CEC [meq/100 g]	Goethite [wt %]	C_{org} [wt %]	$pH_{wa\text{-}ter}$
W1	0.109	0.05	35	112	923	n.a.	n.a.	n.a.	n.a.	4.60
W2	0.271	1.9	26	112	65	n.a.	n.a.	n.a.	n.a.	5.86
W3	0.014	2.0	17	66	41.2	38	2.6	1.80	0.07	5.63
W4	0.367	1.4	<2	<2	2.0	38	9.7	1.57	0.85	4.39
W5	0.006	0.01	34	100	8400	n.a.	n.a.	n.a.	n.a.	5.86
W6	0.351	0.97	40	116	118	n.a.	n.a.	n.a.	n.a.	4.59

n.a. – not available

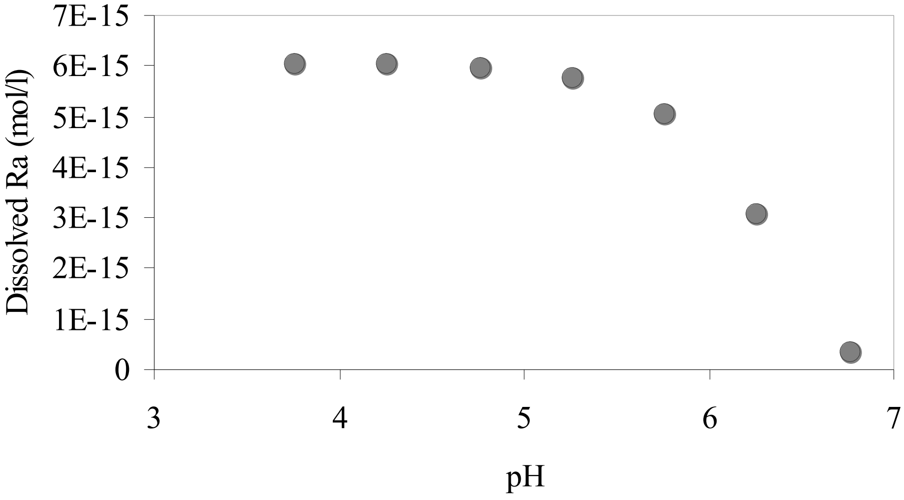
Principal clay mineral was identified as nacrite, a member of kaolinite group. Minerals of this group have relatively low CEC values, in the range from 1 to 10 meq/100 g (Appelo and Postma 1993). Thus, relatively high values of CEC like 9.7 meq/100 g at sample W4 may correspond to a contribution of ferric minerals. Activities of adsorbed radium isotopes are much higher than their dissolved concentrations and ^{228}Ra predominates (Table 5), just like in ground water. Maximum calculated K_d values are high, reaching 8400 L/kg for soil sample from the bottom of borehole W5. Values of K_d as a function of pH are shown in Fig. 4. There is a trend of increasing K_d values for radium with increasing pH. This is consistent with positive charge of dissolved radium and more negative surface charge with increasing pH. The considerable scatter in graph is probably caused by the impact of complexation and by variability in solid phase composition.

Fig 4. Relationship between the value of ground water pH and K_d value.



The adsorption of Ra^{2+} on hydrous ferric oxide (HFO) with composition of goethite was modeled by PHREEQC using the following parameters in diffuse double layer model (DDL): HFO concentration 1.0 wt %, porosity 0.3, bulk density of soil 2 kg/dm^3, and specific surface of HFO equal to 100 m^2/g. This value corresponds to reduced specific surface of goethite (Langmuir 1997) present in soils at the site. Strong adsorption sites density 0.005 mol sites/mol HFO and weak adsorption sites density 0.2 mol sites/mol HFO used by Dzombak and Morel (1990) were scaled down to keep constant site density per nm^2. Intrinsic adsorption constants for barium were used as a proxy for modeling of radium adsorption because intrinsic adsorption constant for radium were not available and adsorption behaviors of both elements are similar (Langmuir 1997). The dissolved Ra concentration in water with pH 3.70 was used as starting concentration because it was assumed that adsorption of Ra concentration was limited at this pH. There was increasing adsorption and, thus, decreasing dissolved Ra concentration with increasing pH (Fig. 5). This behavior was consistent with field observations. This is typical for ferric oxides and hydroxides and supports the hypothesis about their significant role in adsorption of radium. If minerals of kaolinite group were the only adsorbents, there would not have been a significant change in K_d values with pH because their bulk surface charge and adsorption properties do not change very much at observed pH range.

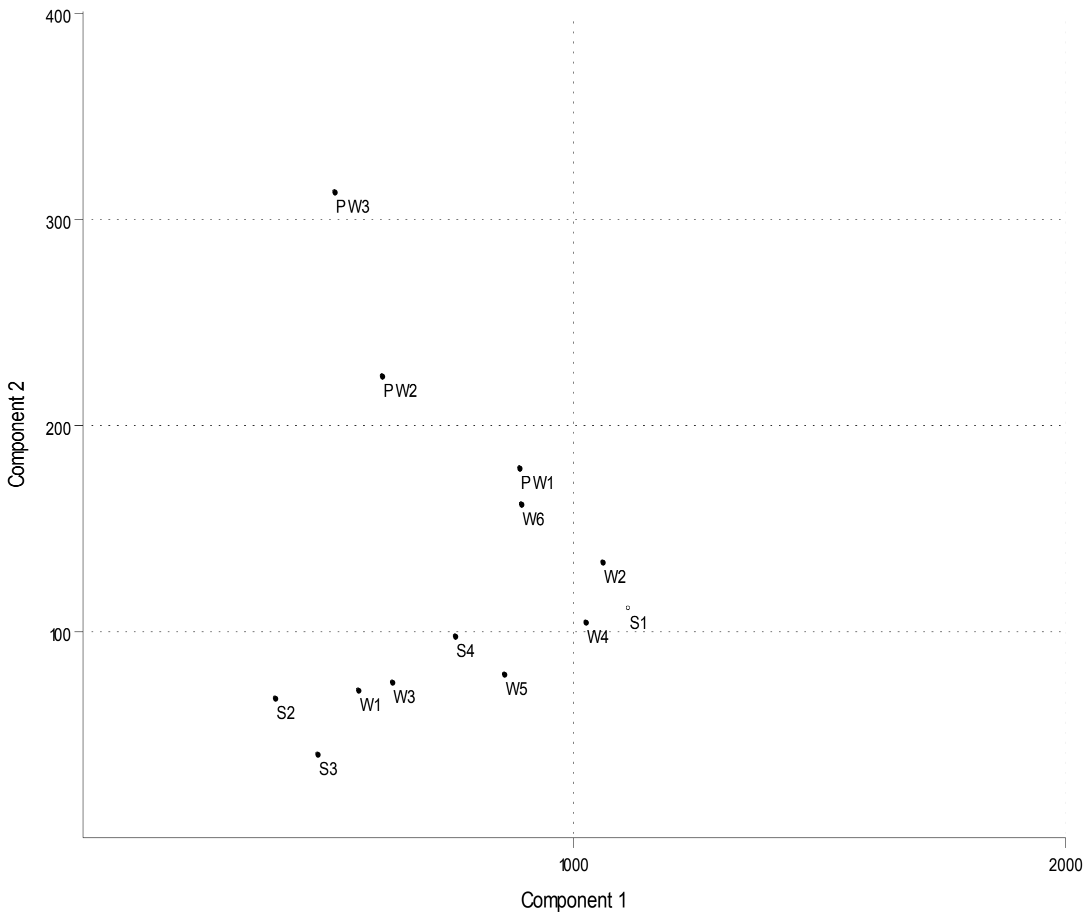
Fig. 5 Modeled concentrations of Ra^{2+} in ground water as a function of pH.



Origin of ground water chemistry and radionuclide behavior

In order to verify the hydrogeochemical similarities among water samples, the data were analyzed using multivariate statistics implemented in the program PAST (Hammer and others 2001). Only principal ions, trace metals, and radionuclides were included, and REE were omitted. Results of Principal Component Analysis (PCA) are in Fig. 6, where loadings of Principal Component 1 (PC1) and Principal Component 2 (PC2) are plotted for all samples.

Fig. 6 Results of Principal Components Analysis (PCA)



The PC1 explains 89 % of total variability and is related to Na, Cl, Mg, and SO_4, e.g., to typical sea water ions. The PC2 explains only 9 % of variability and is not well characterized, comprising Na and K and exhibits relatively low sulfate and chloride concentrations. Samples S1, W2, and W4 are together, representing samples with strong sea water impact. There is evolution towards this end-member from two groups of outsiders: group comprising samples S2 and S3, and group comprising PW2 and PW3. The gradual evolution from samples S2 and S3 towards samples S1, W2, and W4 probably represents increasing influence of marine aerosols. Outsiders PW2 and PW3 may represent ground water of lithogenic origin with limited sea water influence. This is consistent with their high elevation above the Buena Lagoon head.

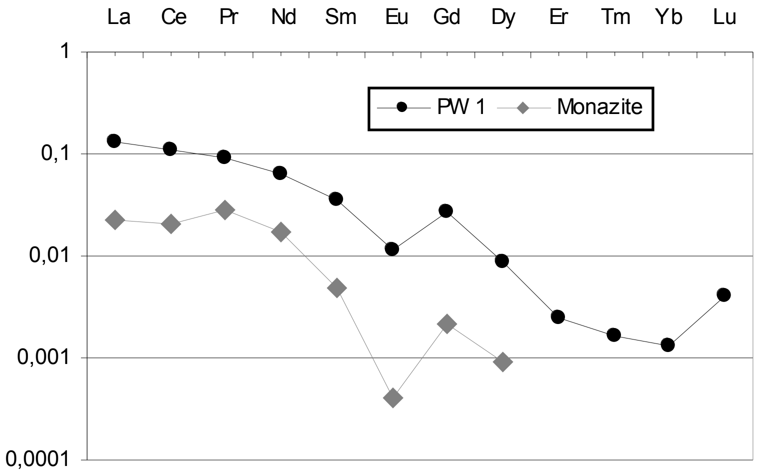
The Pearson correlation coefficient of PW1 and springs variables (Table 6) indicated a strong correlation between light earth rare elements, radium isotopes and Th. The concentrations of ^{226}Ra, ^{228}Ra, and Th were negatively correlated with pH values. Although the concentrations of ^{228}Ra, and U showed good correlation with electrical conductivity (EC), the correlation for ^{226}Ra was weaker (R = 0.717).

Table 6 Correlation among radionuclides and stable elements in ground water samples

Radionuclide	Correlation coefficients (Pearson), significance level >95%.
^{226}Ra	Ce (0.879); La (0.898); Nd(0.830); Pr(0.873); Sm(0.770); H^+ (0.900); ^{228}Ra (0.967); EC (0.717).
^{228}Ra	Ce (0.903); La (0.913); Nd(0.861). Pr(0.897); Sm (0.816); H^+(0.926); ^{226}Ra (0.967); EC (0.800).
U	Nd(0.757); Sm (0.820); conductivity (0.868).
Th	Ce(0.835); La(0.826); Pr(0.840); Nd (0.861); Sm(0.879); conductivity (0.784); H^+(0.803).

The existing relationships between radium concentrations and light earth rare elements concentrations suggest their common origin in ground water, presumably from leaching of monazite. The positive correlation with activity of H^+ and electrical conductivity (e.g., with mineralization) may indicate an important role of these factors in leaching and mobility of radium in aqueous phase. Comparison of the chondrite-normalized rare earth element pattern found in the local monazite to the pattern observed in PW1 sample is in Fig. 7. It is possible to observe that both patterns are quite similar, without a negative cerium anomaly but with a negative europium anomaly. According to Miekeley and others (1992) very low pH values in spring waters result in the presence of cerium as Ce^{+3} under oxidizing conditions. Therefore, the data suggest disturbance of the chemical stability of monazite by high salinity and low pH of ground water.

Fig. 7 **Chondrite-normalized rare-earth element pattern found in the local monazite and the observed in the Private Well I**



General discussion

Two principal factors, high salinity and low pH values, seem to be responsible for high dissolved radium concentrations. The high cation concentrations in ground water (predominantly of Na^+) can result in competition for available exchange sites on solid phase with resulting release of Ra. The low pH values can also increase dissolution rate of monazite, releasing Ra from the solid phase. Furthermore, surface of natural adsorbents of Ra such as ferric oxide and hydroxides has a positive charge under low pH conditions. There is limited adsorption of radium present as Ra^{2+} at low pH values, and adsorption of radium increases with increasing pH (adsorption edge), (Drever 1997). Behavior of uranium and thorium is also related to the presence of their positively charged species such as UO_2^{2+} and Th^{4+} under low pH conditions. When pH values increase, mobility of uranium and thorium is reduced due to adsorption. However, the trend is reversed for uranium at close to neutral pH values due to the formation of carbonate complexes (Langmuir 1978; His and Langmuir 1985). Furthermore, there is inhibition of thorium adsorption by formation of complexes with sulfate (Riese 1982). On the other hand, formation of relatively strongly adsorbed thorium hydroxy-complexes like $Th(OH)_4^0$ is limited in low pH samples. Phosphate released by monazite dissolution is in anionic form and is adsorbed on positively charged surfaces at low pH range. There also is a possibility of precipitation of phosphate minerals like strengite ($FePO_4.2H_2O$) and variscite ($AlPO_4.2H_2O$), (Robertson and others 1998), in the proximity of dissolving monazite because concentrations of Fe^{3+} and Al^{3+} in ground water are relatively high.

Conclusions

Ground water close to the head of Buena Lagoon in coastal zone of Rio de Janeiro state exhibits high salinity and generally low pH values. Probably the most significant factor playing role in formation of ground water chemistry is the influence of marine aerosols, resulting in high concentrations of Na and Cl in ground water. Strong correlation between concentrations of radium and LREEs suggests leaching of monazite as a common source. Factors responsible for high radium mobility in ground water seem to be high salinity with resulting competition for adsorption sites, and low pH values with resulting limited adsorption of Ra^{2+} on the surface of adsorbents like ferric oxide and hydroxides. Behavior of uranium and thorium is also influenced by their speciation and generally low pH conditions. Uranium is present as positively charged uranyl ion

UO_2^{2+} under low pH conditions and is very mobile. Carbonate uranium complexes predominate in some samples with close to neutral pH and mobility of uranium increases again. Positively charged Th^{4+} and thorium complexes with sulfate predominate in low pH samples with relatively high concentration of thorium. Further study should be focused on the aquifer delimitation, as well as on causes of low pH values.

References

Almeida RMR, Lauria DC, Ferreira AC, Sracek O (in press) Groundwater radon, radium and uranium concentrations in Região dos Lagos, Rio de Janeiro State, Brazil. Journal of Environmental Radioactivity

Appelo CAJ, Postma D (1999) Geochemistry, groundwater and pollution, A. A. Balkema Brookfield Rotterdam

Beneš P, Obdržálek M, Čejchanová M (1982) The physicochemical forms of tracers of radium in aqueous solutions containing chlorides, sulfates and carbonates. Radiochem. Radioanal. Letters 50/4: 227-242

Beneš P (1984) Migration of radium in the terrestrial hydrosphere. The behaviour of radium in waterways and aquifers. Technical Reports Series No.310, International Atomic Energy Agency. IAEA-TECDOC-301 Vienna. pp119-173.

Carnet A, Jacquemin R (1990) Methods for measuring radium isotopes: Gamma spectrometry. The environmental behaviour of radium. Technical Reports Series No.310, International Atomic Energy Agency, IAEA-TECDOC-301 . Vienna. pp189-204

Drever J I (1982) The geochemistry of natural waters. Prentice Hall, Englewood, New Jersey

Dzombak DA, Morel FMM (1990) Surface complexation modeling: Hydrous ferric oxide. John Wiley and Sons, New York

Embrapa (1997) Manual de métodos de análises de solo/Centro Nacional de Pesquisa de Solos,2rd. Embrapa, Rio de Janeiro

Godoy JM, Lauria DC, Godoy MLDP, Cunha RP (1994) Development of a sequential method for the determination of 238U, 234U, 232Th, 230Th, 228Th, 228Ra, 226Ra, and 210Pb in environmental samples. Journal of Radioanalytical and Nuclear Chemistry Articles 182(1): 165-169

Hammer Ø, Harper DAT, Ryan PD (2001) Past: Paleontological Statistics Software Package

for Educational and Data Analysis. Paleontologia Electronica 4 (1)

His CKD, Langmuir D (1985) Adsorption of uranyl onto ferric oxyhydroxides: application of surface complexation site-binding model. Geochimica et Cosmochimica Acta 49: 1931-1941

Kraemer TF, Reid DF (1984) The occurrence and behavior of radium in saline formation water of the U.S. Gulf Coast Region. Isotope Geoscience 2:153-174

Krauskopf KD (1986) Thorium and rare earth metals as analog for actinide elements. Chem. Geol. 55: 323-335

Langmuir D (1978) Uranium solution-mineral equilibria at low temperatures with application to sedimentary ore deposits. Geochimica et Cosmochimica Acta 42:547-569.

Langmuir D, Herman JS (1980) The mobility of thorium in natural waters at low temperature. Geochimica et Cosmochimica Acta 44: 1753-1766

Langmuir D, Riese AC (1985) The thermodynamic properties of radium. Geochimica et Cosmochimica Acta 44:1753-1766

Langmuir D (1985) The thermodynamic properties of radium. Geochimica et Cosmochimica Acta 49:1593-1601

Langmuir D (1997) Aqueous environmental geochemistry. Prentice Hall, New Jersey

Lauria DC, Godoy J M O (2002) Abnormal high natural radium concentration in surface waters. Journal of Environmental Radioactivity 61(2): 27-37

Lauria DC, Almeida R M R, Godoy J MO, Sracek O (2002) On the high radium concentrations and low pH values in ground waters of a Brazilian coastal region. Proccedings of the International Conference on Radioactivity in the Environment, Monaco, CD-ROM.

Miekeley N, de Jesus HC, da Silveira CL, Linsalata P, Morse R (1992) Rare-earth elements in groundwaters from the Osamu Utsumi Mine and Morro do Ferro analog studies sites, Poços de Caldas, Brazil. Journal of Geochemical Exploration 45: 365-387

Parkhurst DL (1995) PHREEQC: A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. U.S. Geological Survey, Lakewood, Colorado

Parkhurst DL, Appelo CAJ (1999) PHREEQC-2, A Hydrogeochemical Computer Program, U.S. Geol. Survey, Water Resour. Invest., Lakewood, Colorado

Riese AC (1982) Adsorption of radium and thorium onto quartz and kaolinite: A comparison of solution/surface equilibrium models, Ph.D. thesis, Colorado School of Mines, Golden, CO

Robertson WD, Schiff SI, Ptacek CJ (1998) Review of phosphate mobility and persistence in 10 septic systems plumes, Groundwater 36:1000-1010

Standard methods for examination of water and wastewater (1975) 14rd edn. American Public Health Association Washington

ENVIRONMENTAL ASSESSMENT OF THE MATERIAL DEPOSITED ON THE FORMER URANIUM MINING DISPOSAL DUMP IN RADONIÓW. (POSTER)

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Introduction

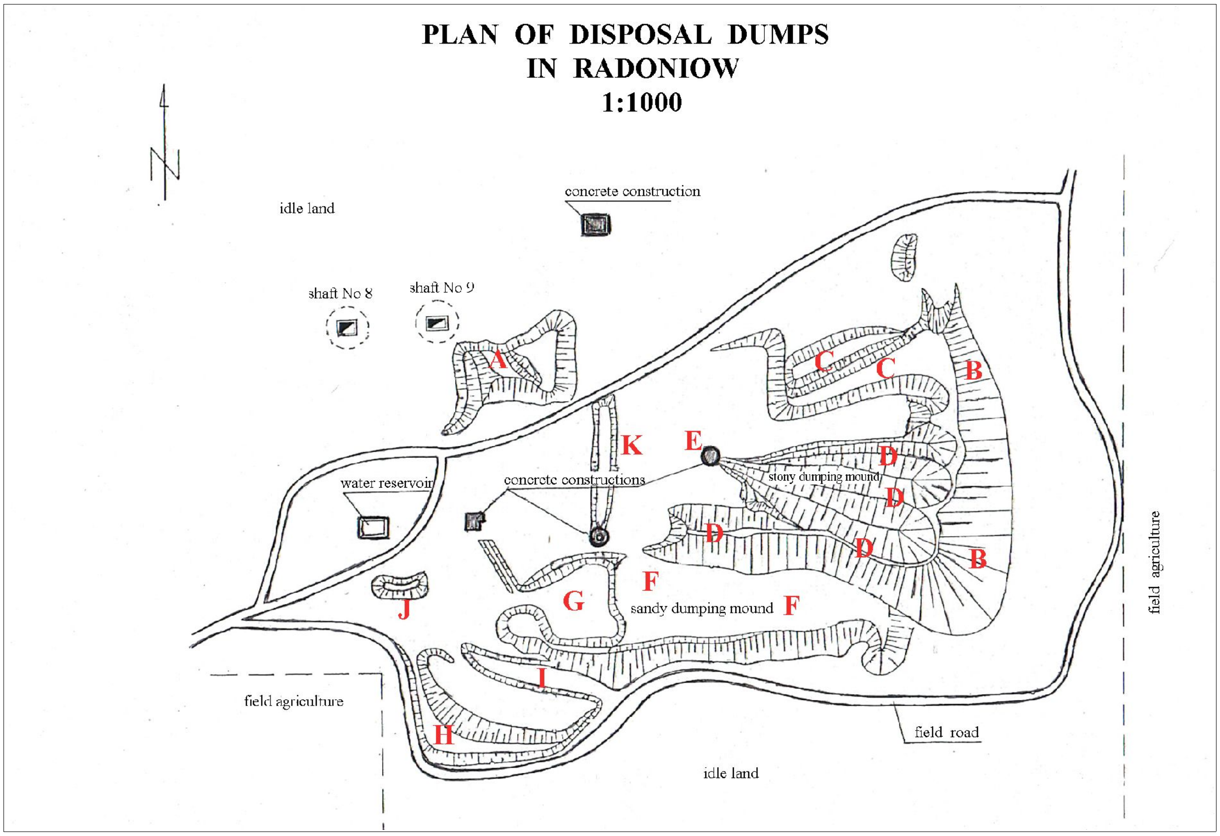
Radoniów is a small town located in Lubomierz district near Jelenia Góra (south-west part of Poland). Since the end of World War II up to the end of sixties there were uranium mining activities in the vicinity of the town. Uranium deposits were almost entirely exploited and the traces of the mining activities are the post-

uranium dumps on the east side of mount Głębiec. The area of the terrain is about 6,85 ha. The material present on the dumps (containing high amount of uranium) is to be – according to the plans of the district authorities - used as the bedding for the construction of the road around the town (PHARE contract).
The measurements performed by the Central Laboratory for Radiological Protection (CLOR) and ordered by MOSTOSTAL-Warszawa (developer of the road) were to asses the usability of the dumped material for road construction.

Description of the area

The plan of the area, which comprises of the several dumping mounds, is presented in Figure
Main part of the dump is surrounded by the field road. North of this part of the dump the idle land is situated. On this area, next to the shaft no. 9, small steep dumping mound with irregular top (A) is located.
Eastern part of the dumping site is limited by the high dumping mound (B) stretching along south-north axis. This mound is connected with two smaller ones (C) having flat top and three steep stony dumping mounds (D) in the direction towards concrete construction (E). At the foot of the high stony dumping mound (D) the sandy flattened covered with birch forest dumping mound (F) is situated. At its west side circular reentrant is seen (G). In the south-west part of the area, close to the road, the narrow sickle-shaped embankment (H) is located, and further north the flattened part (I) going into small valley, behind which there is promontory of the sandy dumping mound.
Small few meters high dumping mound (J) is located in the western part of the area.
Between concrete construction and the external road there is a long dumping mound having plain ridge (K).

Fig. 1. Plan of disposal dumps in Radoniow.



Measurement program and methods.

The assessment program consisted of:

- environmental measurements at the disposal site (dumps) of the uranium mine in Radoniów;
- assessment of the usability of the materials from the dumping site for the construction of the circular road passing by Radoniów (part of the state road No. 30);
- analysis of the risk for the workers having contact with the material deposited on the dumps in Radoniów.

The following tasks were performed:

Measurement of the whole area by the mobile spectrometric laboratory (creating the radiological map of the area).

The Mobile Spectrometric Laboratory is based upon Toyota Land Cruiser GX90. The scintillation detector type Exploranium GPX-256 with the NaI(Tl) crystal having the volume of 4 liters (dim. 16” x 4” x 4”) is mounted on the roof of the car. The detector is placed in the aluminum container and covered with the polyurethane foam. Its task is to permanently measure the environmental gamma spectra, both along the measuring route and while standing. The Mobile Spectrometric Laboratory is also equipped with the GR-660 system mounted on the back seat of the car in the special shockproof container. The GR-660 system consists of the on-board computer with touch screen connected to the computer with a long cable. Such connection allows the operator to sit on the front seat of the car. The computer stores the collected measurement data and performs the on-line visualization. The second element of the GR-660 system is 256-channel spectrum analyzer Exploranium GR-320 connected to the detector placed on the roof of the car. In addition, the car is equipped with the differential Geographic Positioning System (DGPS) allowing very precise determination of the position of the car (within 0.5 meters). The results from the GPS are transferred to the on-board computer. The measuring route is presented on the screen. Further they allow preparing the radiological maps.

The GR-660 spectrometer allows the determination of the presence of natural radionuclides at the following levels:

- potassium ^{40}K – 0,13% (40 Bq/kg)
- uranium – 1,6 ppm (20 Bq/kg)
- thorium – 1,0 ppm (4 Bq/kg).

The results of the measurements are stored on a HDD of on-board computer. Further elaboration of the data is performed in the laboratory using specialized software for detailed spectra and auxiliary data analysis, e.g. creation of radiological maps of the investigated area.

Measurements of gamma dose rate in 41 measuring points and collecting gamma spectra in 5 points (3 points on the investigated area and 2 neutral points representing natural background) using Exploranium GR-130 handheld spectrometer.

Hand-held nuclide identifier Exploranium miniSpec GR-130 is equipped with NaI (Tl) detector for the determination of dose rate, search for the sources and collection of the gamma spectra. For the measurements in the high-dose fields it has GM detector. When the dose rate becomes high, the device automatically switches to use GM for dose rate measurement. Gamma spectra can undergo qualitative analysis for nuclide identification. All results are stored in the memory of the device for further transfer to the computer and analysis.

Measurements of beta radiation above the dumped material the surface of the dumped material and measurement of gamma dose rate with RKP-1 radiometer.

The activity of the beta radiation above the material dumped in Radoniów was measured by means of standard RKP-1 radiometer calibrated with ^{90}Sr source. The method of the measurement consists in counting the pulses from beta and gamma radiation while the detector window is open and then counting the pulses with closed detector window. The difference gives the count rate which originated from beta radiation. The dose rate is measured with closed detector window switching the device mode to dose rate measurement.

Measurement of dose rate in 5 points by means of ionization chamber.

Dose rate was measured also by means of the current-type pressurized ionization chamber. The chamber is made of high-pressure steel tank of 5-liter volume and wall thickness of 4 mm. The pressure of argon gas is 35 atmospheres. The tank is covered by 1.5 mm of aluminum preventing from the noise. The self-counting of the chamber is 2 nGy/h. The VA-J-51 electrometer equipped with dynamic capacitor powered with AC 220 Volts or accumulator (in field) is used to measure the current. The calibration of the instrument was performed assuming that terrestrial background of gamma radiation is in 70% equivalent to the radiation ^{226}Ra source filtered by 0.5 mm of platinum and in 30% the radiation of ^{131}I source. Calibration procedure took into account the influence of scattered radiation, directional anisotropy of the ionization chamber and the attenuation of the radiation in air.

The value of background dose rate $\dot{D}$, 1 m above ground was calculated using the following equation:

$$\dot{D} = VK - \dot{D}_0 \quad [nGy/h]$$

where:

V – the velocity of the rise of charge on the dynamic

$V = \frac{z}{t}$ *[mV/s]*, where: *z* – voltage rise on the capacitor during measurement,

t – voltage rise time(time of measurement) – average of 5 readings;

K – calibration coefficient $\left[\frac{nGy/h}{mV/s}\right]$ determined during calibration procedure,

$\dot{D}_0$ - self-counting (background) of the chamber *[nGy/h].*

Dose rate is determined with ± 10% error.

Sampling for further laboratory analyses in Dosimetry Department of CLOR (gamma spectrometry with natural contamination analyzers - AZAR-90 an MAZAR-95)

The following samples were taken:

- 41 samples of the surface material of the dump (10 cm depth);

- 10 samples from the deep layers of the dump (taken by the specialized geological company “Geological Services”);
- 2 samples representing local natural environment.

Every surface material sample was averaged from 5-7 subsamples taken from the central point and from the circumference circle of diameter of 2 meters.

The method applied for the determination of the activity of the samples is based upon comparison of concentrations of natural radionuclides: potassium ^{40}K, radium ^{226}Ra and thorium ^{228}Th. It consists in the analysis of the count rate registered in three channels – separately for the examined sample and three volume calibration sources of potassium, radium and thorium.

The count rate is measured by means of scintillation detector with three-channel amplitude analyzers AZAR-90 and MAZAR-95.

The scintillation detector is located id the lead shielding chamber. The walls of the shielding are 50 mm of lead and 2 mm of steel. The Marinelli beaker containing the sample (1,7 dm^3) is placed inside the chamber. The task of the chamber is to reduce external gamma background. Such geometry allows to achieve more counts in the defined measurement time. The detector is powered by stabilized high voltage power supply. Pulses from the detector are processed in linear amplifier and passed to one of three single-channel analyzers. In addition, inside the chamber there is ^{137}Cs source for controlling of the slope of calibration curve..

Every single-channel analyzer is set to its energy range:

- Range I: 1,26 – 1,65 MeV covering potassium ^{40}K with energy 1,46 MeV;
- Range II: 1,65 – 2,30 MeV covering mainly pulses of energy 1,76 MeV of bismuth ^{214}Bi from uranium-radium series;
- Range III: 2,30 – 2,85 MeV covering mainly pulses of energy 2,62 MeV of ^{208}Tl from thorium series.

The pulses from the outputs of every analyzer are counted separately, and the results are stored in three memory groups. The device is supplied from 230 V AC.

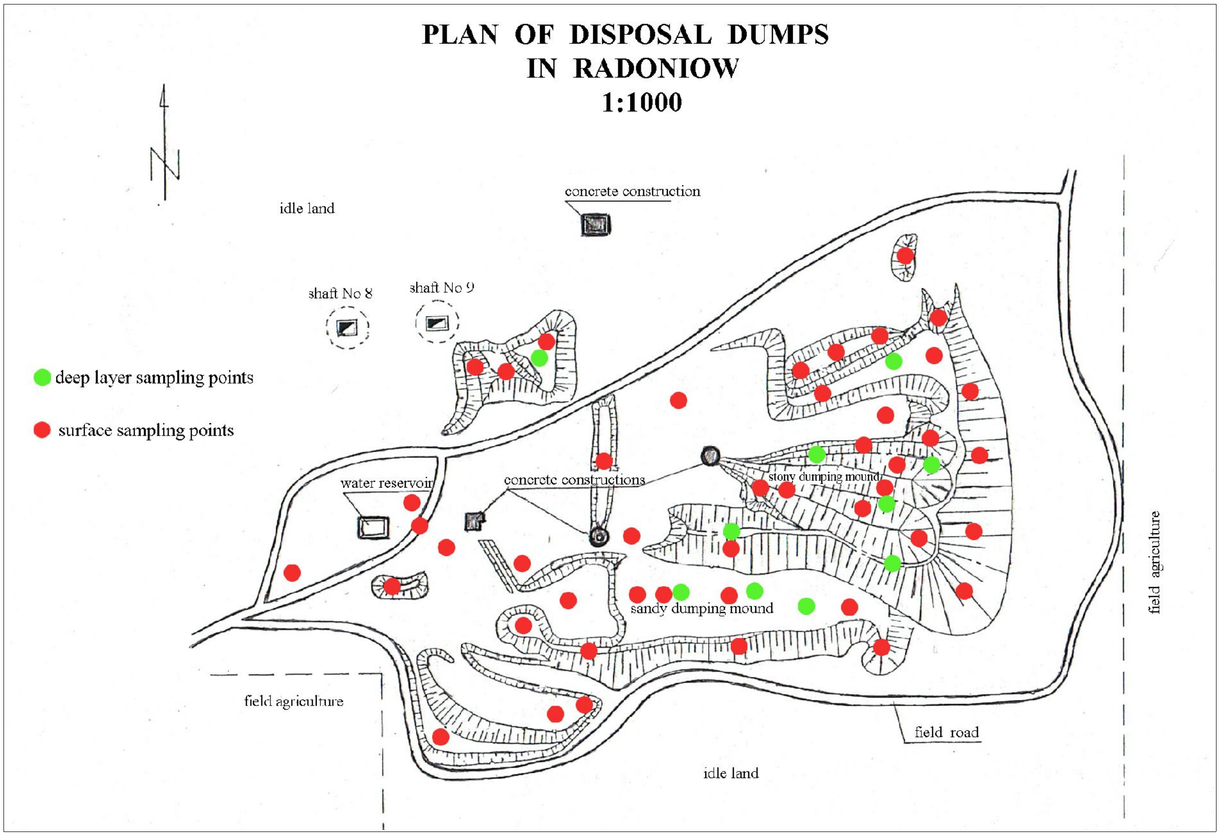
The measurement technique of potassium ^{40}K, radium ^{226}Ra and thorium ^{228}Th is described in detail in the "*Guidelines on the Determination of Natural Radioactivity in Raws and Building Materials*", Instruction 234/2003 of Institute of Building Technology.

Basing upon measured concentrations of potassium ^{40}K, radium ^{226}Ra and thorium ^{228}Th the values of radioactivity indices f_1 and f_2, and the dose rate above flat indefinite plane of thick (few meters) layer of the measured material are calculated.

Results of measurements

The distribution of all measurement and sampling (surface and deep) points is presented in Figure 2.

Fig. 2. Measurement and sampling points



The results of surface beta radioactivity measurements.

The results of the surface beta radioactivity fall within the range between 0.16 Bq/cm^2 and 1.92 Bq/cm^2, having average at 0.52 Bq/cm^2. All measured values are less than 3,7 Bq/cm^2, i.e. limit value for beta surface radioactivity for laboratories applying beta radionuclides. The comparison is due to lack of the norms on permissible beta activity values in natural environment.

The results of the concentration of natural radionuclides in samples taken from the dumping mounds.

The measurements of the environmental samples were performed in Natural Radioactivity Section of Dosimetry Department of CLOR.

The measured concentrations of natural radionuclides ^{40}K, ^{226}Ra i ^{228}Th are presented in Table 1.

Table 1. Concentration of natural radionuclides in surface- layer soil samples.

Nuclide	Nuclide concentration [Bq/kg]			Place maximum concentration occurred*)
	average	range	in neutral points	
^{40}K	1627	782 – 5704	740; 686	a, b, c
^{226}Ra	2172	252 – 8726	95; 49	b, c
^{228}Th	95.3	37.5 – 782.4	38.5; 36.0	a, b, c

*) Description of places of maximum concentration:

a – between road and concrete construction near water reservoir;

b – between road and water reservoir;

c – west part of dumping mound A (at its top).

The values of f_1 and f_2 coefficients calculated basing upon measured radionuclide concentrations are given in Table 2. The values were calculated according to Regulation by Council of Ministers of 3 December 2002 (Law Gazette no 220/2002 pos.. 1850).

Table 2. Values of f_1 and f_2 coefficients.

Coefficient [unit]	Value			Place maximum value occurred *)
	average	range	in neutral points	
f_1 [-]	8.26	2.33 – 34.90	0.76; 0.57	b, c
f_2 [Bq/kg]	2172	252 – 8726	95; 49	b, c

*) *Description of points b and c like in Table 1.*

The results of gamma dose rate measurements.

The values of gamma dose rate measured in the dumping area are given in Table 3.

Table 3. Gamma dose rate values

Instrument	Gamma dose rate [nGy/h]			Place maximum dose rate value occurred *)
	average	range	in neutral points	
Radiometer RKP-1	680	300 - 1800		a, b, c
Exploranium GR-130	662	288 - 1988	142; 117	a, b, c

*) *Description of points a, b and c like in Table 1.*

The measurements performed in some points by the ionization chamber confirmed the correctness of the results obtained by other methods.

Additional environmental spectrometric measurements were made by Mobile Spectrometric Laboratory. The measurements were performed along the roads which allowed driving by all-terrain car. The concentration of potassium, thorium and uranium was measured. The detector is situated 2 meters above ground, so the measurements do not represent point values but are averaged from larger area. Thus the results may have exclusively approximate meaning indicating the places having elevated natural radionuclide concentration.

Analysis of the results of measurements

Analysis of possible application of materials for construction

Legal basis

In Poland, for the purpose of evaluation of raw and building materials for use in constructions of various types, the criteria given in the Regulation of Council of Ministers of 3 December 2000 "*on natural radioactive isotope content I raw and building materials used in buildings for population and livestock, as well as in industrial wastes used in construction, and monitoring of the concentration of these isotopes*", Law Gazette no 220/2002 pos. 1850 (later called Regulation) are applied.

According to the Regulation the concentration of the natural radioactive isotopes in raws and building materials, as well as wastes is calculated using:

- activity coefficient f1 defined by equation

$$f_1 = \frac{S_K}{3000} + \frac{S_{Ra}}{300} + \frac{S_{Th}}{200}$$

- activity coefficient f2

$$f_2 = S_{Ra}$$

where: S_K, S_{Ra}, S_{Th} are the concentrations of potassium ^{40}K, radium ^{226}Ra and thorium ^{228}Th, in Bq/kg.

§3 of the Regulation states that the values of f_1 and f_2, cannot exceed 20% of the following:

1. $f_1 = 1$, $f_2 = 200$ Bq/kg related to raws and building materials applied in construction for public or livestock;
2. $f_1 = 2$, $f_2 = 400$ Bq/kg related to industrial wastes used in surface constructions situated on the ground and built on the inhabited (used) areas or devoted for construction in the local urbanization plans, and for leveling of such terrains;
3. $f_1 = 3{,}5$, $f_2 = 1000$ Bq/kg related to industrial wastes for constructions situated on the ground not mentioned above and for leveling of the terrains not mentioned above;
4. $f_1 = 7$, $f_2 = 2000$ Bq/kg related to industrial waste used in underground parts of constructions mentioned in point 3 and in underground constructions such as railway and road tunnels excluding industrial wastes used in underground mining galleries.

§4 of the Regulation determines, in addition, that while using industrial wastes for the leveling of the terrain quoted § 3 pt. 2 and 3, and for road, sports and recreation object construction it should be assured that achievement required values of f_1 and f_2 will cause the absorbed dose rate at 1 meter above terrain, road or object be less than 0.3 microgrey per hour (300 nGy/h), in particular by putting the additional layer of another material.

The recommended procedures on sampling and preparation of samples, measurement, and elaboration of the results can be found in the "*Guidelines on the Determination of Natural Radioactivity in Raws and Building Materials*", Instruction 234/2003 of Institute of Building Technology.

Analysis of the measurement results

Obtained results of f_1 and f_2 coefficients given in Table 2 proved that:

- None of samples the satisfies the requirements of w §3 pt. I of the Regulation,
- 2 samples satisfy §3 pt. 2,
- 12 samples of not satisfying §3 pt. 2 satisfies §3 pt. 3,
- 19 samples of not satisfying §3 pt. 3 satisfies §3 pt. 4,
- 18 samples does not satisfy §3 pt. 4.

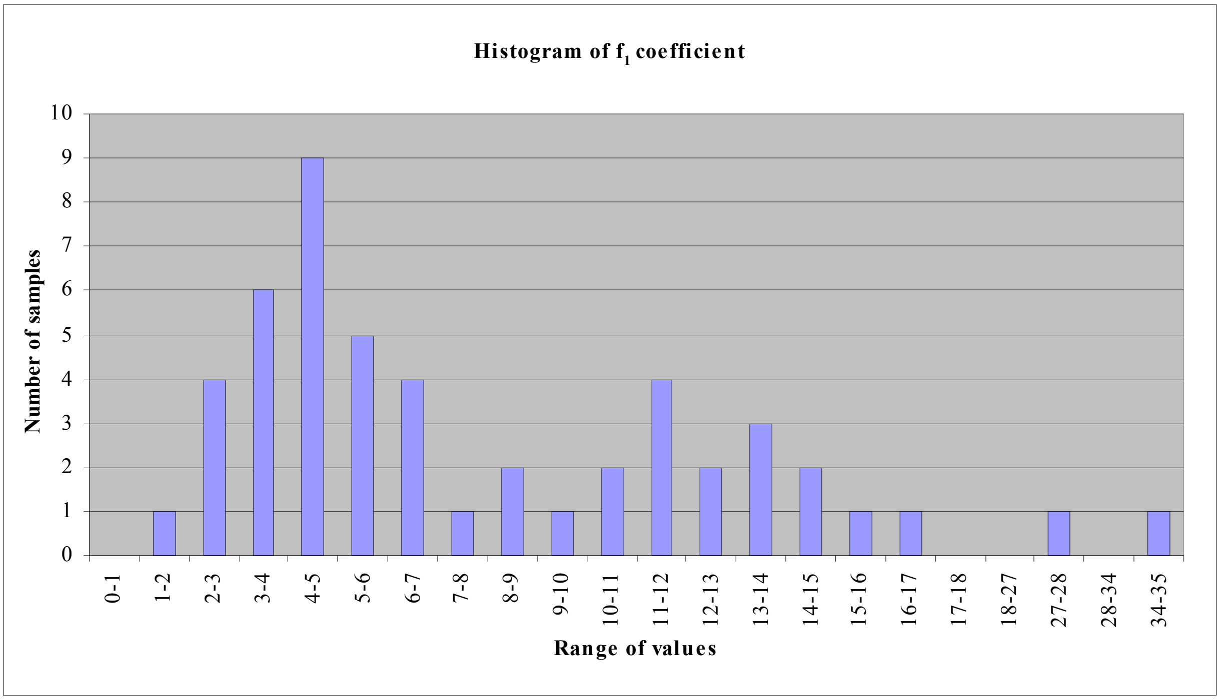


Fig. 3. Histogram of f_1 coefficient.

The histograms of f_1 and f_2 coefficients that are presented in Figures 3 and 4 show that there are probably two groups of materials present in the area: :

- first, with f_1 ranging from 0 to 9 and f_2 from 0 to 2500 Bq/kg,

- second, with f_1 ranging from 9 do 16.4 and f_2 from 2500 to 4332 Bq/kg.

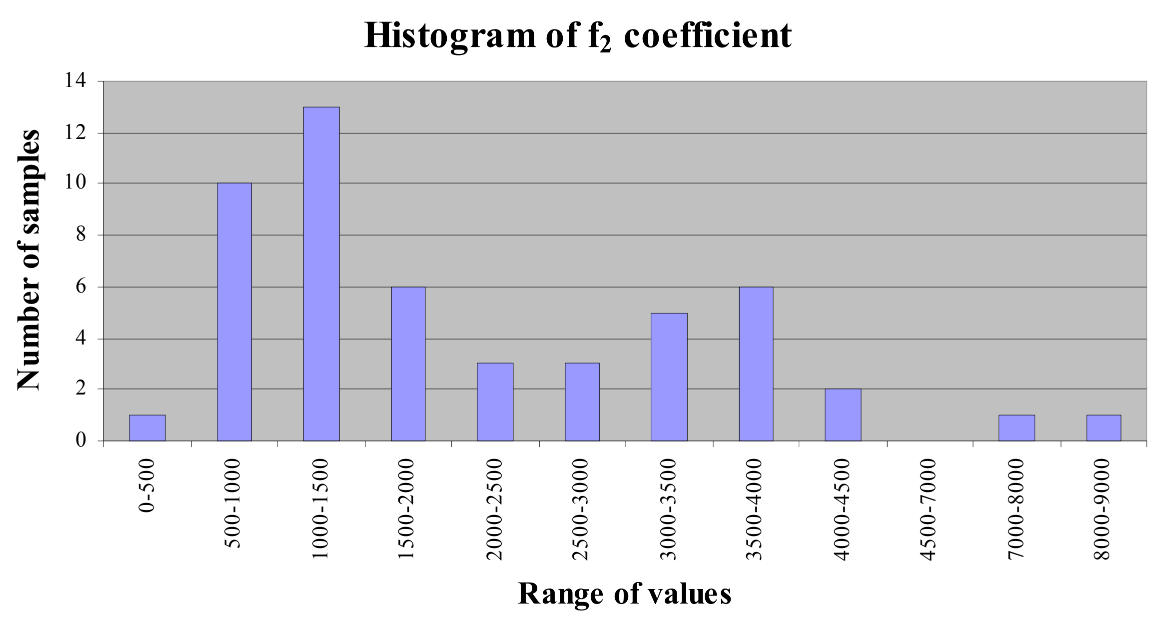


Fig. 4. Histogram of f_2 coefficient.

In addition, there are two “hot spots” in the sites described as b and c – see table 1 (for point b: f_1 = 27.9; f_2 = 7083 Bq/kg; and for point c: f_1 = 34.9; f_2 = 8724 Bq/kg). The possibility remains for other “hot spots” (having small, few meter diameter) to exist in the area, which were not included for sampling. Thus, it is recommended to check the site with simple dosimeter.

Analysis of ionizing radiation risk for the employees working with the materials from the dumps.

Legal basis

The fundamental legal act is “Atomic Law” of 29 November 2000. The Act is the set of general regulations. The article no 13 is most important in our case.

„Art. 13

Dose limit is the sum of doses from external and internal exposure.

Dose limit does not include exposure to natural radiation, when not increased by human activities; in particular do not include exposure to radon in dwellings, exposure to natural isotopes in the human body, cosmic radiation at ground level, and exposure over the surface of the earth from radioactive isotopes present in intact earth crust."

The values of dose limits of ionizing radiation for specific population groups are given in the Regulation by Council of Ministers of 28 May 2002 “on limiting doses of ionizing radiation” (Law Gazette no 111 pos. 969).

Analysis of the exposure for workers in the examined area.

Values given in §5 of the Regulation by the Council of Ministers of 28 May 2002 applies for the employees working by the circular road construction passing by Radoniów. According to the regulation, dose limit for such persons, expressed as effective dose is 1mSv per calendar year. The dose can be exceeded during the year if during 5 following years its value does not exceed 5 mSv.

The exposure to beta and gamma radiation was taken into account.

For this analysis workers employed on the dump and the construction of the road were divided into two main groups:

- Employees working in the cabins (excavators, bulldozers, trucks etc.),
- Employees directly on the dump and road (non-shielded).

It was assumed:

- Nominal exposure time 2100 working hours in a year,
- Wearing overalls and rubber boots,
- Maximum values of surface beta activity and gamma dose rate (excluding “hot spots”).

The results of analysis of the exposure of workers are presented in Table 4. The exposure for ionizing radiation ranges from 0.90 mSv/year to 2.54 mSv/year. Most exposed workers are those working directly on the dump in places not satisfying the Regulation by Council of Ministers of 3 December 2002 §3 pt. 4. Least exposed workers are those in cabins either on the dump or on the road in places conforming to the above point of the Regulation. It should be stressed that all exposure values (for specified groups of workers and workplaces) were calculated taking into account maximum values of exposure factors, so real exposure would be lower. This analysis does not include exposure for persons at “hot spots”.

Environmental protection

The concentration of radium on the dump (excluding “hot spots”) exceeds 3 to 50 times the concentration of radium in the vicinity of the dump. Thus, it is recommended to protect the environment by the dump material:

- Maximum limitation of dusting during excavation of the material;
- Protection of material loses during transport:
- Sprinkling transported material with water or
- covering transported material with foil,
- Maximum limitation of dusting during construction of the road,
- Refraining from organizing of the intermediate dumps.

Table 4. Results of analysis of exposure of workers.

Group of workers	Scope of activities	Exposure place	Exposure factors		Annual exposure time [h]	Beta effective dose [mSv/year]	Gamma effective dose [mSv/year]	Total exposure at workplace [mSv/year]
			beta radiation [Bq/cm2]	gamma dose rate [nGy/h]				
workers exposed on the dumps and by the construction of the road not shielded by the walls of specialized vehicles	work on dumps	sites not complying with par. 3 pt. 4	1,36	1064	2100	1,17	1,56	2,54
		sites complying with par. 3 pt. 4	0,64	742	2100	0,55	1,09	1,45
	work by road construction	sites complying with par. 3 pt. 4	0,64	742	2100	0,55	1,09	1,45
workers exposed on the dumps and by the construction of the road shielded by the walls of specialized vehicles	work on dumps	sites not complying with par. 3 pt. 4	negligible	1064	2100	1,17	0	0,98
		sites complying with par. 3 pt. 4	negligible	742	2100	1,09	0	0,9
	work by road construction	sites complying with par. 3 pt. 4	negligible	742	2100	1,09	0	0,9

Conclusions

The following conclusions are drawn basing upon the measurements on the site, the samples collected from Radoniów post-uranium disposal dumps and analysis of the exposure to workers:

- Material on the disposal dumps is inhomogeneous with respect to concentration of natural isotopes: particularly ^{226}Ra: from 252 Bq/kg to 8724 Bq/kg. Neighboring points with totally different concentration of ^{226}Ra were found. Highest concentration of radium is at “hot spots” . This material shall not be used in any applications, and shall be recultivated on-site. Remaining material can be used for road construction after mixing with material having low natural isotope concentration so that the final product complies with the Regulation of 3 December 2002 (§ 3). It shall be stressed that the road built using this materials shall comply additionally with § 4 requirements i.e. reducing absorbed dose rate at 1 meter above road surface to the value not exceeding 300 nGy/h;
- The exposure of workers employed directly on the dumps and road construction (not shielded by cabin walls) will result in dose of from 1.45 mSv to 2.54 mSv (2100 hours of work per year), so it will exceed value of I mSv/year. However, according to the Regulation of Council of Ministers “on dose limits”, dose limit at 1 mSv in calendar year can be exceeded, provided that in following five years summed 5mSv dose would not be exceeded. Thus, for the period of the construction of the road less than 2 years the limitation of working hours below 2100 h is not mandatory. The exposure will not exceed 1 mSv for the workers employed as operators of special building vehicles.

IMPROVING CRITERIA FOR REMEDIATION OF MONAZITE BY-PRODUCTS CONTAMINATED SITES IN BRAZIL

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Abstract

In 1999 the first Brazilian decommissioning process occurred in São Paulo State at a monazite physical and chemical treatment plant, closed down since 1992. The decommissioning process comprised equipment, piping, buildings and land decontamination with the final site release for unrestricted use. At the present time, another monazite site is being decommissioned in the same State. Regulations for intervention situation in mining and milling of ores with uranium and thorium associated are being developed now, due to this, the

decommissioning activities have been based on case-by-case analysis and ALARA criteria. Investigations are being made to propose suggestions for public participation in the process and establish a method of working together, in order to obtain a more effective communication between regulatory agency and society.

This paper presents an overview on the situation of three sites in São Paulo State: a past and a present remediation case and a site to be decontaminated in the future. All sites presented contamination with radioactive residues produced by outdated monazite chemical processing. We also propose some proceedings improvement based on past experience and international guidelines. This paper also suggest the implementation of public participation in the remediation process evaluation.

Introduction

One of the thorium occurrence is in beach monazite sand. These sands are found at large extension of Brazilian coast, from the northern border of Rio de Janeiro State to south of Bahia State. Monazite is an orthophosphate of thorium and rare earth -(Ce, La, Y, Th)PO_4- and contains an average of 6% ThO_2, 0,3% U_3O_8 and 50% to 60% rare earth oxides. The Brazilian practice for monazite treatment was made in two phases. First the monazite was separated from silica and other minerals (ilmenite, rutile, zircon) by a combination of gravity, electrostatic and magnetic separation techniques. A concentrate containing more than 90% of monazite was obtained. In this physical phase of the process no relevant waste was produced. In the second phase the monazite was attacked by sodium hydroxide solution in autoclaves, transforming the mineral into water-soluble trisodium phosphate and mixed hydroxides of rare earth and thorium. Then the rare earth elements were solubilized by hydrochloric acid (pH 3,5 – 4,0) and separated from thorium hydroxide by filtration.

Figure 1 shows the chemical processing of monazite which took place in Brazil until 1992, resulting in two main radioactive by-products:

- thorium hydroxide concentrate, a precipitate named cake II (20% ThO_2, 1% U_3O_8), with specific activity around 1820 Bq/g; and
- barium-radium sulphate crude residue, a precipitate named mesothorium (Ba (Ra) SO_4), with specific activity around 4360 Bq/g .

Cake II retains most of thorium and uranium from monazite. For each 100 tons of monazite chemically processed, 2 tons of cake II and 7 tons of mesothorium are produced [1]. There aren't any estimate for total number of cake II and mesothorium produced in Brazil from 1949 to 1992. Monazite chemical process phase produces large quantities of residues with low level long lived natural radionuclides from ^{238}U and ^{232}Th series.

Regulatory Aspects

The chemical processing of monazite sands to produce rare earth began to be explored in São Paulo State in 1949, before National Nuclear Energy Commission (CNEN) establishment in 1956 (Decree 40110/56) and, almost 30 years before of the Brazilian Institute of the Environmental and its Resources (IBAMA) set up, in 1989 (Law 7735/89), with the responsibility by the environmental licensing. This kind of industry produced large quantities of radioactive by-products according to the process described above. Regulations for intervention situations in mining and milling of ores with uranium and thorium associated are being developed by CNEN. The draft version is available in CNEN internet site. [2]

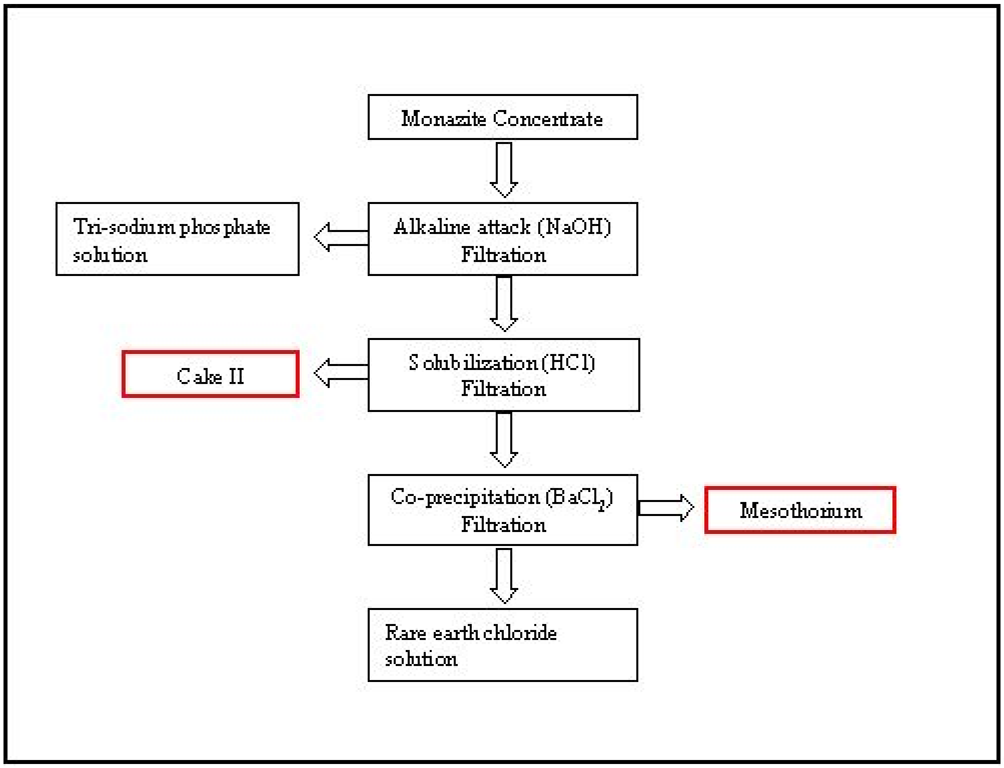

Figure 1: Monazite Chemical Process

In accordance with the Brazilian Nuclear Policy Act (Law 4118/62 as amended by Law 6189/74 and 7781/89) CNEN has the responsibility to establish regulations and implement nuclear policy. The Licensing and Control General Co-ordination Board of CNEN is responsible for performing regulatory control of nuclear facilities: issuing licenses, authorising construction, operation and decommissioning. The Brazilian Environmental Policy Act (Law 6938/81 as amended by Law 7804/89 and 8028/90) was enacted almost 20 years after the Brazilian Nuclear Policy Act.

It is IBAMA's responsibility, the environmental licensing of undertakings and activities with significant environmental impact in the national or regional scope, that includes search, mine, treat, store and dispose of radioactive material in any step, or activities that use nuclear energy in any of its forms and applications, according to CNEN's evaluation.

IBAMA will carry out the licensing process after considering the technical evaluation made by the State and Municipal environmental agencies, where the activity or undertaking is established, as well as the evaluation of the other pertinent Federal, State or Municipal agencies involved in the licensing process. (CONAMA 237/97)

Case 1:

A monazite processing plant named USAM (Usina de Santo Amaro), located at São Paulo, started operation in 1949 and closed down in 1992. The site with an area of 11000 m^2 consisted of three units: physical separation of raw mineral, chemical treatment of monazite and rare earth separation.

The justification for intervention was:

- along the years the place turned into an urban area,
- from 1979 on, with the evolution of radiological protection concepts, the site has showed as critical point the inadequate dust generation control system, as well as a limited storage capacity of by-products - cake II and mesothorium. [3]

The decommissioning process begun in 1994 in the physical unity, the simplest one. The adopted proceedings included radiological characterisation of the site, equipment and constructions decontamination, material classification considering the final destination: reuse, landfill, scrap sale or radioactive waste, in accordance with CNEN regulations.[4]

The higher risk areas were the area of monazite milling, due to dust deposition, and the area of chemical treatment. CNEN surveyed the dismantling and the decontamination activities, the workers doses were below the limits and there were no accidents while the work was being done.

The waste generated in the process was transferred to another site, located near the facility, which is presented here as case 2. The authorisation for this temporary storage was given in 1995 by Environmental Agency of São Paulo State. (CETESB)

The site release for unrestricted use was based on a conservative residential scenario, considering all exposure pathways for a dose limit 1mSv/y to derive an activity concentration level 600 Bq/kg ^{228}Ra. Before release a final survey was conducted by CNEN to confirm the release criteria adequacy.

As it was the first decommissioning to take place in Brazil it was done under critical and diligent CNEN evaluation not only to guarantee the established limits, but all safety criteria. The process ended in 1999.

Case 2:

This site is now under decommissioning process. It is located in São Paulo city, with an area around 60.000 m^2, of which 4.500 m^2 were occupied by 3 storage sheds: A, B and C, and 55.500 m^2 land area with weedy vegetation. Storage shed A (2060 m^2) is being used as temporary storage for the waste generated in the decommissioning case 1. Storage sheds B e C, with no activity since 1992, were demolished in 2002, under CNEN survey.

In the past the owner first used the site for storage of residues of mineral processing, and then for a period of time storage shed A was used as a rare earth extraction unit.

Two contamination sources were identified at the soil site: monazite sand and cake II. Investigations are in course to verify if there is underground water contamination.

Case 3:

From 1975 to 1981, 3500 tons of cake II were stored in seven concrete constructions, built especially for this purpose, in a rural property located is São Paulo State, in a farm region. A river crosses the property and flows to a station, that supplies with water a city 12 km away. The local population is very concerned about the situation.

Monitoring programs executed in the site revealed two areas presenting with ^{226}Ra contamination and two others with ^{228}Ra. In august 1983 technicians of local environmental agency recorded an activity concentration of 0,8 Bq/L ^{226}Ra in a well located inside the site. In march 1993 the same well showed a value of 4,0 Bq/L. Since 1989 the well was sealed.

At the moment a soil characterisation is being made in the site using a triangular grid of 11 m, in accordance with MARSSIM methodology [5] to determine the contamination extension.

The property owner hasn't shown interest yet in decommissioning the site. In case the owner intends to keep it as a storage, very detailed studies must be developed.

Public Participation

In spite of the importance of the nuclear industry, laymen always associate radiation to weapons, war and accidents. Although its most harmful consequences are rare, this is incomprehensible to most citizens.[6]

The first release of an urban site in São Paulo for unrestricted use until todays induce questions to CNEN. It is clear that non radiological factors affected the public. Perhaps, if during the decommissioning process, public representation have been involved, acceptance of the results would had been enhanced with a decisive influence in the final release. Dialogue can increase support for decisions, although it is a lengthy process.

Final Remarks

Remediation is a complex process. We propose the adoption of an integrated strategy (Figure 2) in which the justification of the remediation action will be based not only on impact criteria, but also in a social and economic approach to obtain an optimisation of decision making process. An effective contamination land management adopting the environmental legislation, considering the evaluation of the other pertinent State or Municipal agencies and authorities involved in the licensing process is suggested.

This strategy propose four preliminary steps:

- a diagnostic of public perception;
- a diagnostic of stakeholders interests;
- an effort to establish a link between technical and social evaluation;
- to define a methodology to consider social and local authorities engagement.

Until the moment there is no disposal site for this low level long life waste in Brazil. CNEN is selecting an adequate site for this permanent storage.

Specific regulations or guides concerning decontamination and decommissioning are necessary to advise evaluation actions.

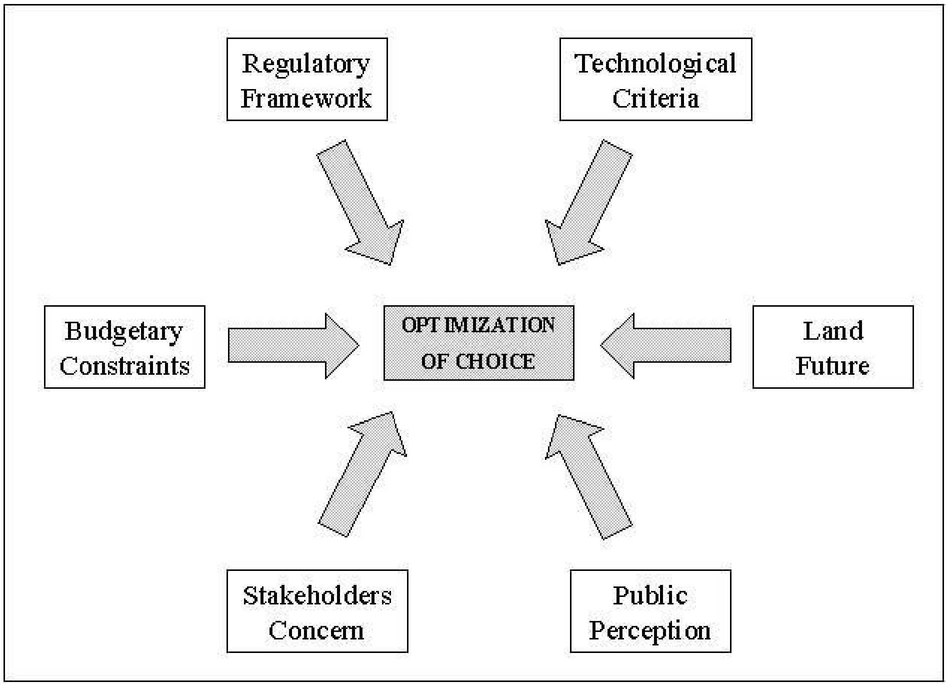

Figure 2: Remediation Evaluation Framework

References

1. Paschoa, A Potential Environmental and Regulatory Implications of Naturally Occuring Radioactive Materials Appl. Radiat. Isto. Vol 49 (3) 189-196, 1997
2. CNEN website: www.cnen.gov.br
3. Silva, K. M et al "Critérios de Radioproteção aplicados no Descomissionamento da USAM", ENAN, 1997.
4. CNEN NE 6.05 Management of Radioactive Wastes in Radioactive Facilities, 1985
5. NUREG 1575, NRC/EPA/DOE Multi Agency Radiation Survey and Site Investigation Manual (MARSSIM), august 2000

6. Siqueira, M.M. et al. “Percepção de Riscos e de Impactos Sócio-econômicos da Radioatividade”. FAPEMIG Project Research Report - SHA 243/2002. 2003. 53p.

DISMANTLING OF A NORM CONTAMINATED PHOSPORIC ACID PLANT IN THE NETHERLAND

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1. Introduction

The Netherlands does not have phosphorous acid plants anymore. The last two plants, operated respectively by Norsk Hydro (Hydro Agri, Rotterdam B.V.) and Kermira BV have ceased to produce in the year 2000, after which their dismantling was started. In the Netherlands the production of phosphorous acid started in the beginning of the last century, and this has been continued during the whole century. In the seventies it was observed that with the production of phosphorous acid radioactive deposits could occur in the production installations.

The applied chemical process, the used phosphorous ores, and a number of physical parameters determined the type, and extent of the depositions.

Sedimentary phosphorous ores only contain small concentrations of Uranium-238 in equilibrium with its decay products, amongst which is Radium-226. The concentration depends on origin, and composition.. As a result of the chemical process salts with Radium-226 come into being that are deposited in certain parts of the process installation. Because of the process Uranium-238 remains in solution, and is found in the phosphorous acid. By adjusting the chemical process, and process parameters, and changing the type of phosphorous ore that was used, one succeeded to reduce the radioactivity problem considerably. The older installations had radiation levels up to100 μSv/hour, and activity concentration of Ra-226 up to 1,500 Bq/gram.

2. No new generation

At the end of the seventies, and the beginning of the eighties there was more and more attention drawn on the risk of exposure from ionising radiation, including the exposure from naturally occurring radioactive materials (NORM). In the nineties, also the risk for the environment due to the exposure to NORM was investigated. In the second half of the nineties the first regulations were drawn up for non-nuclear industry. Companies from this industry had to obtain a license if the activity concentration of the depositions in their installations was higher than 100 Bq/g. Change of policy by the Dutch government in the area of waste, and problems with the sale of by-products such as gypsum on the market led to considerable problems. As a consequence the companies no longer invested in the modernisation of their phosphorous acid plants. At least in the Netherlands there were no good perspectives anymore for the future.

In accordance with the Euratom directive 96/29 of May 13th, 1996, a new Dutch Radiation Protection Ordinance came into force on July, 16th, 2001. In this new ordinance a chapter was introduced exclusively applicable for work activities involving naturally occurring radioactive materials. It is expected that a regulation based on this chapter will come into force by the end of 2004. The proposed regulation was send to the European Commission for verification in the beginning of 2004.

3. The dismantling of the phosphorous acid plant of Hydro Agri Rotterdam B.V.

3.1 Plan of action

Problems can occur with the maintenance and dismantling of process installation, in which NORM deposits exist as a result of the use of radioactive raw materials. Exposure to these radioactive substances can lead to health risks for the personnel involved as a result of inhalation, ingestion, and external exposure. Therefore, in the Netherlands according to the Radiation Protection Ordinance a license is required to perform these work activities.

Because of the required specific knowledge of the process, and the risks involved with these NORM contaminated installation, they are in general dismantled by the personnel of the owner. Permission is required from the Dutch authorities before dismantling can take place. The company that carries out the dismantling has to have a license. Only after the whole dismantling is finished, and all obligations in the license are fulfilled, the license of the company can be withdrawn.

Before the dismantling takes place a plan of action has to be drawn up with a description of the most inportant health and safety aspects, and the impact for the environment, taking in to account the economic aspects. Such a plan of action contains the following:

- The necessary preparations (flushing, putting out of operation)
- The organisation of health and safety, and responsibilities
- The way of disposing of radioactively contaminated installation parts, and radioactive substances
- The way of dismantling of the installation
- The way of use of the technical equipment in the dismantling of the installations
- The way in which (radioactive) waste is treated
- The disposal of waste

The plan of action must contain a risk inventory in which the exposure of workers, and the environment are estimated. Moreover a description must be given on how this exposure is kept as low as reasonably possible. During the dismantling, the plan of action has to be adjusted as it turns out that the information that was used in drawing up the original plan, is superseded.

3.2 The final report as a dossier.

At the end of the dismantling a report has to be presented with the following contents:

- historical information and references
- a summary of the whole project
- the organisation with respect to responsibilities, and supervision
- the applicable licenses
- the results of the preliminary inventory
- an overview of the identified contaminated installation parts
- an overview of the applied methods for treating these parts
- the plan of action for each method
- an overview of the released contaminated parts after

- an overview of the release of the used equipment
- an overview of the applied, and released tools and aids
- a calculation of the dose received by the workers, and the environment
- an overview of the quantities and temporary storage of produced (radioactive) waste
- the transfer of radioactive substances to third parties for the purpose of further processing

The report must be available for at least 15 years. The document may be used in evidence.

3.3 Technical Approach

In the case of dismantling of a NORM contaminated installation it is advised to start with the performance of a radiation survey. During the survey the whole installation has to be measured, and all the radiation level have to be recorded, and arranged. With this information the objects that are responsible for the highest radiation levels are identified and if these levels limit the radiation survey of the other parts of the installation.

The installation part that can be dismantled or can be decontaminated elsewhere can now be selected. Next a plan is drawn up to remove or clean objects with the highest radiation levels. As a result the radiation level in a certain area is lowered, and other objects with a enhanced radiation level can be identified in a second survey. With the information from this second survey, again the objects with the highest radiation level can be removed, and “new” contaminated objects become “visible”.

Radioactively contaminated metal objects, that could not be decontaminated properly can be transferred to an metal foundry that has a license to melt these objects. In the Netherlands it is allowed to export such objects for this purpose. Objects that can be decontaminated, or that can not be transferred to the metal foundry, onsite decontamination is the best option. From experience it is known that the radioactive deposits that occur with the production of phosphorous acid in general can be removed with the use of high pressure or ultra high pressure (> 2,500 bar) water jetting. In general the released radioactive substances (scales) are not very soluble in water.

During decontamination with water little particles occur with variable diameters in the range from 0.1 micrometer up to some millimetres. In general the activity concentration as a function of the diameter is constant. This means that the used water can be cleaned with available separation techniques. In most of the cases the water remains contaminated with non radioactive components. Therefore, in the Netherlands it is not allowed to discharge the used water in the surface waters.

Installation parts that come in contact with acid normally are protected by a coating or with a rubber-lining. As a results of the contact with the acid, radioactive deposits occur in the top layer of coating and the rubber. During the project also the rubber has to be decontaminated with high pressure water jetting. With this method a long rubber belt of the belt-filtersystem, including the accompanying transportation reel could treated. The radioactive contamination could be milled away, by applying a suitable combination of nozzles, pressure, and amount of water.

The reactor vessels, and acid storage tanks also have protective layers. The reactor vessels had a layer consisting of rubber on carbon stones that were glued to each other. The acid storage tanks had a rubber coating. Because of the long period in which the vessels and tanks were used, the surfaces were contaminated with deposits containing Radium-226. With the use of a robot the surfaces have been decontaminated with high pressure water jets. The robot could be moved horizontally and vertically across the surfaces to which it is attached by producing a vacuum that was also used to drain away the water with the radioactive particles to a storage tank. The radioactive particles were removed from the water afterwards. When using water under high pressure a mist occurs. This mist was removed through a filter system by a vacuum installation. Discharging of the water-air mixture is done via a demister, and an absolute filter. Because of these measures discharge of radioactivity in the environment has been very limited.

4. End results of the project

4.1 Exposure of personnel and environment

Exposure of the persons as a result of:

- The wet decontamination: 1,2 mSv
- The dry decontamination: < MDA
- Dismantling/construction activities, and assistance: < 1,7 mSv
- Supervisors: <MDA

Exposure of the environment, risk for the public outside the plant site

- Maximum < 0,4 μSv (risk < 10^{-8})

4.2 Work activities with respect to the removal and disposal of radioactive substances

Decontamination I:

Wet decontamination; with high pressure water jetting the following objects could be decontaminated:

- Reactor vessel (transformation)
- Reactor de-fluorising
- Storage tank for soft acid
- Stainless steel frame and transport reels of a belt filter system
- Rubber belt of the belt filter, with the exemption of the centre strip of 10 cm.
- Buffer tank (spilled acids)
- Seal tanks, and table filter
- Remaining part of the tilting-pan-filter
- Metal constructions, machine frames and smooth part of the installations
- Ceramic tiles that were used on the floor
- Drains and gutters
- Carbon (stones) from the coating of the reactor
- Some drain wells

Decontamination II:

Dry decontamination; with stainless steel grit blasting the following objects were decontaminted. Because of disappointing results, the decontamination of the filter plates, funnels and the table filter by blasting has been ceased because of distortion of the objects

- Filterplates and funnels, table filter (20.000 kg)

4.3 Work activities

Dismantling, transport, storage, and other activities

- Pipes, pumps, funnels

5. Treatment and transfer of radioactive objects and waste by third parties

5.1 Melting

Installation parts that could be melted were packed in closed IP-1 containers for treatment elsewhere. Objects that were to big, such as tanks, were cut in pieces before they were packed. In total seven containers were removed. The following installation parts were melted:

- Parts of the tilting-pan filter
- all steel pipes (with rubber lining)
- seal tanks
- separators
- buffer tank

5.2 Transfer of radioactive materials

- 62 tons of steel packed in 7 containers were melted at the German company Siempelkamp. The total activity was 1.9 GBq Ra-226, and 0.5 GBq Pb-210
- 6.711 kg of radioactive waste was transferred to the Dutch Central Organisation for Radioactive Waste (COVRA) packed in 118 barrels of 100 litre. It concerned carbon waste, NORM scales, and rubber waste with a total Ra-226 activity of 7 GBq
- The HEPA filters that were used during the decontamination were also transferred to COVRA.

Remark: The radioactive waste had to meet the specification of COVRA that the liquid content should be smaller than 1%. Therefore the waste was dried by an infrared installation before packing.

5.3 Industrial waste

- 447,990 kg of water with radioactive particles that was used in the high pressure water jetting system (collected in 16 tank cars). This water was first treated (cleaned) by an industrial waste company and then handed over and treated as chemical waste because of the present other chemical (solible) components. The remaining radioactivity concentration was less than 1 Bq/liter (Ra-226).
- Scales (gypsum), to be treated as chemical waste 750.000 kg (< 1 Bq/gr Ra-226)

6. Stock of raw material

- The stok of phophorous ores has been sold.

7. Recycling of other materials

- 2,213,000 kg of scrap metal was transferred to scrap metal traders in 129 containers. In two of these containers some activity was found by a portal detector at the entrance gate of the scrap yard.

8. Tranfer of machines to third parties (sale)

- Belt filter installation, The Netherlands (without rubber belt, and filter cloth)
- Table filter, Greece

9. Information regarding Health, Safety, and Environment

9.1 Used filter systems for guarding water and air

- Produced mist, and used air

Step 1: demister

Step 2: absolute filter (HEPA)

- Water used in high pressure water jetting

Step 1: several pre-filters

Step 2: settle tank

Step 3: filter units: 100 µm – 1 µm – 0.5 µm

Step 4: re-circulation with addition of coating: < 0.5 µm

9.2 Air measurement with filters, type GF/B15:

- Maximum measured alpha concentration: 1.8 Bq/m^3
- Total calculated discharge in air: < 34 kBq

10. Incident reports (decontamination)

- No personal incidents
- Small leakage filter system (neither personal, nor financial risk)
- A person did not receive proper instructions
- Two container with radioactively contaminated scrap were transferred to a scrap metal trader (violation of the Nuclear energy act)
- Leaking pump, extra cleaning of the area (small personal risk, small financial risk)
- Overflow of tank, extra cleaning of the area (no personal risk, small financial risk)

RADIOLOGICAL IMPACT ON THE UK POPULATION OF INDUSTRIES WHICH USE OR PRODUCE MATERIALS CONTAINING ENHANCED LEVELS OF NATURALLY OCCURRING RADIONUCLIDES: ZIRCON SANDS INDUSTRIES

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Introduction

In the European Union the revised Basic Safety Standards, as defined in Council Directive 96/29/EURATOM (European Commission, 1996), provides a regulatory control system for the protection of workers and the public from sources of ionising radiation. In the case of exposure to natural radiation sources, other than to radon, national authorities may determine which work activities require controls. There is, however, a need for harmonisation of the regulatory control of natural radiation sources within the EU. In 1999 the National Radiological Protection Board (NRPB) and the Centre d'Evaluation de la Protection Nucleaire (CEPN) performed a study to identify possible reference levels for the regulatory control of workplaces involved in the production or processing of materials containing enhanced levels of naturally occurring radionuclides (European Commission, 1999). Following this report, NRPB initiated a project to investigate the radiological impact of non-nuclear industries in the UK.

This paper describes the fourth report in the series of reports by the NRPB on the radiological impact of non-nuclear industries within the UK which process or produce materials containing enhanced levels of naturally occurring radioactive material (NORM). It considers the exposures from the production and use of zirconium compounds from zircon sands (Oatway et al, to be published). The report considers the radiological impact of the primary industry, the waste streams produced, the normal use of the products and, where applicable, the uses of by-products.

The ores from which these chemicals are extracted contain the naturally occurring radionuclides ^{235}U, ^{238}U and ^{232}Th and their decay products. Some of the production processes are such that most of the radioactive material present in the raw materials passes through to the final product, while some products are essentially free of radioactive material. The aim of the study was to consider all exposures that could arise from the time when the raw material is imported into the UK to the time when all activity has been disposed of.

Description of the industry

Zircon sand is the basic material for a wide variety of uses, particularly in refractory materials and glazes. Natural zircon sand has a particle size that can be up to a few hundred micrometers, which is too coarse for many of the applications. The first step in the processing of zircon is therefore to grind it to an appropriate particle size, producing what is known as zircon flour. This is done using dry processes when producing particle sizes of tens of micrometers, and wet processes for finer particles. These processes are not considered to remove any of the activity from the original raw material. Doses to workers and members of the public from this part of the industry are considered.

Once milled, the zircon flour is packed into bags, which are either exported or used in other manufacturing steps by other companies within the UK. In general, users of zircon flour "simply" empty the contents of the bags into machines used by their industry. Much of the flour is used as a paste and in general the doses to the workers in these factories are likely to be considerably lower than to those workers in the milling process. However, the doses to workers who empty the bags of zircon flour may not be trivial as there can be a considerable amount of airborne material released during this step of the process. Hence the doses to workers emptying bags of zircon flour are considered in this study, but doses from other stages are not.

Zircon sand is also used as the raw material for the manufacture of zirconium chemicals. The chemical processing essentially removes all the radioactive material from the products and so the doses from the use of the products are extremely small, and are therefore not considered in the report. The radioactive material removed from the product, which has the same relative amounts of different radionuclides as the raw material, is disposed of as waste. Doses to workers in the factory, and to members of the public from waste disposal, have been considered.

Zircon can also be fused with other chemicals to modify some of its properties for some applications. This process (termed fusion) involves heating zircon sand to a high temperature, combining the product with other materials, followed by a grinding process to produce “flour” at the required particle size. The fusion process raises the temperature to a point where it is likely that the radon, lead and polonium are removed from the product. Air filters installed in the furnace gas treatment plant will trap most of the dust released by this process, but there will be some discharge of material to the environment. Doses from this part of the industry are considered. Doses from the subsequent use of the flour produced are likely to be lower and so are not considered in this study apart from the doses whilst emptying bags of material during later product manufacturing. In this case, the exposure is considered to be the same as that described above from exposure to emptying bags of zircon flour from the milling process.

The relationships between the various stages of the zircon sand industry, as described above, are presented in Figure 1. This provides an overview of the industry with arrows indicating the passage of material between the various industrial stages. Also shown are the principal waste streams considered in the report, although for simplicity not all streams are shown.

Source term

It was assumed that the activity concentration of the material during processing was equal to that of the raw material for most of the assessment calculations as the activity is considered not to change significantly during milling. From measured activity concentrations in materials that are used in the industry in the UK (personal communication, P Shaw), the typical activity concentrations are:

^{238}U chain members	3000 Bq kg^{-1}
^{232}Th chain members	600 Bq kg^{-1}
^{235}U chain members	150 Bq kg^{-1}

These values are intended to represent material used by the industry in the UK in general and hence some generalisation has been made. For comparison, a study by the EU (European Commission, 2001), which looked at clearance and exemption within Europe for industries which may have potential problems with naturally occurring radionuclides, found typical activity concentrations of uranium and thorium in zircon sands of 5000 Bq kg^{-1} and 1000 Bq kg^{-1} respectively. It should be noted that most areas of the industry in the UK are now specifically obtaining raw material from sources that have low activity concentrations.

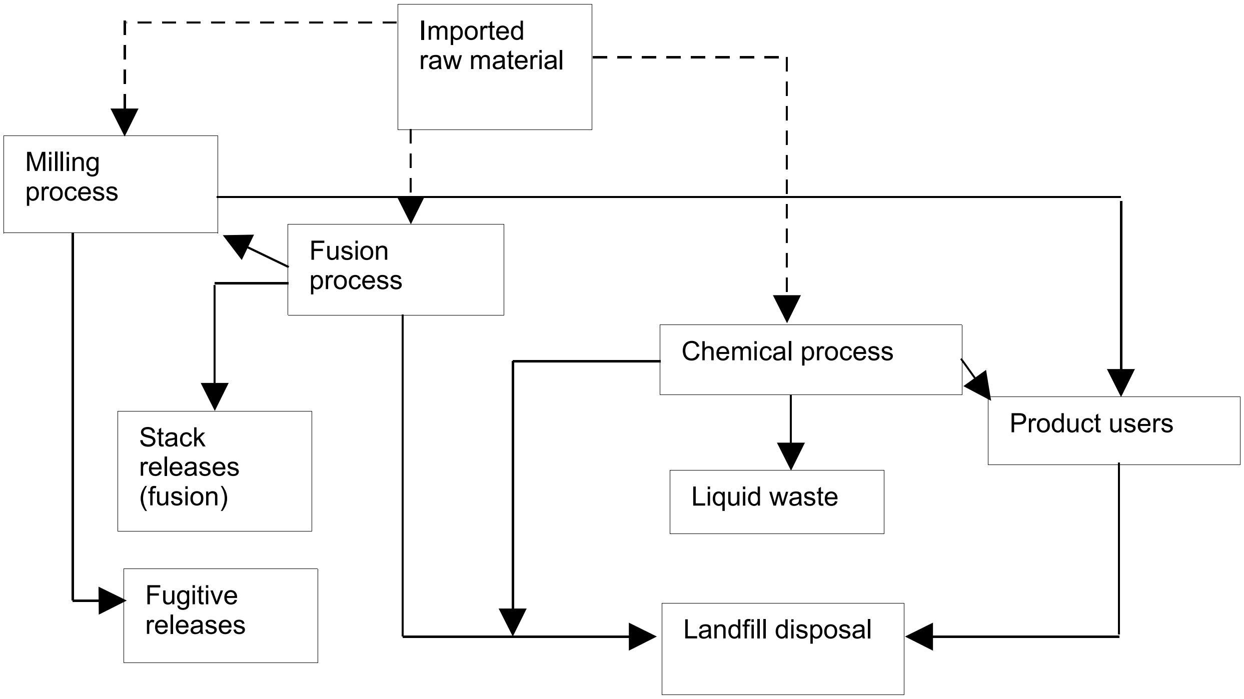

FIGURE 1 Schematic overview of the zircon sand industry in the UK showing the main processing and waste stream steps

In a limited number of cases, exposures will be to material with an activity concentration that is different to the raw material, for some radionuclides. Examples are those who work with material released during the high temperature (fusion) processes. In such processes it is possible that some radionuclides

(^{210}Pb and ^{210}Po in particular) will become volatilised and collect in filter and extraction systems designed to clean air before it is released to atmosphere. Material in these situations is considered to have an activity concentration of (personal communication, P Shaw):

^{238}U chain members (apart from ^{210}Pb and ^{210}Po)	1500 Bq kg^{-1}
^{210}Pb	10 000 Bq kg^{-1}
^{210}Po	10 000 Bq kg^{-1}
^{232}Th chain members	600 Bq kg^{-1}
^{235}U chain members	150 Bq kg^{-1}

Exposure groups considered

The study considers the exposure to both workers in the industry and to members of the public from disposal or release of waste products. All workers have been assessed where it was thought that exposure could not be disregarded from a radiological protection point of view. The workers assessed included those involved in transporting material in lorries and those workers involved in the milling and fusing of material. The exposure times selected are taken to represent the general activities of a single worker throughout the year, and include times spent near bulk material as well as times spent near to machinery or bagging final product. Doses have also been assessed from dust present on the overalls worn by the workers, and to other people who are involved in cleaning them.

Exposures to members of the public are from three waste streams. Atmospheric releases have been considered for both general wind-blown emissions and for releases from fusing of material. Exposure to liquid wastes is considered when the waste is discharged into a local river where boating may occur. Exposure has also been considered for material disposed of to landfill. In this case, doses from exposure for both present day and future site occupants have been considered. The exposure groups and the pathways considered are shown in Table 1.

Doses to workers from processing and manufacturing items from zircon sand

The doses to workers are summarised in Table 2, which considers doses to transport and laundry workers and three types of process workers. Also presented in the table are the dominant pathways for each exposed worker and the percentage contribution that pathway makes to the total dose. The "raw material process" workers are those workers involved in the milling of zircon sand and any other workers who are exposed for an entire year to material with an activity concentration that is not altered from the raw material. The "fusion process workers" are those involved in the fusion part of the industrial process. They are exposed for most of the year to material which has an activity concentration equal to the raw material, but are also exposed to material from the fusion dust collection system for limited periods of time. The "manufacturer workers" are those in subsequent industries (such as end-product manufacturers) where the main exposure to radioactive materials comes during the opening of bags of zircon flour or sand and their insertion into a processing line. The item labelled “laundry workers” is the dose to people who handle dirty work overalls during cleaning.

TABLE 1 Exposure pathways considered

People considered	Pathways considered
Transport worker	External irradiation during transport
Process worker (representing milling and fusion workers)	External irradiation from stored materials and from material in the plant undergoing treatment Internal irradiation from the inhalation of airborne material Internal irradiation from the inadvertent ingestion of material in the plant undergoing treatment Internal irradiation from the inhalation of radon from stored materials

Manufacture workers	External irradiation from material in the plant undergoing treatment Internal irradiation from the inhalation of airborne material
Laundry workers	External irradiation from contaminated overalls Inhalation of material resuspended from contaminated overalls
Members of the public from atmospheric releases	External irradiation from the material in the plume and that deposited on the ground from the plume Internal irradiation from the inhalation of material in the plume (including radon) and that resuspended from material deposited on the ground from the plume Ingestion of food grown in land upon which material from the plume has been deposited
Members of the public from liquid discharges	External irradiation from material in the water whilst canoeing Internal irradiation from material inadvertently ingested whilst canoeing
Members of the public from the disposal of solid waste (present day) – landfill workers[*]	External irradiation from disposed material in the ground Inhalation of suspended material during disposal Inadvertent ingestion of disposed material External irradiation from material present on the skin
Exposure of future users of a landfill site from solid waste disposal	External irradiation and internal irradiation from inhalation and ingestion of material from constructing buildings on the landfill site in the future (excavation) External irradiation and internal irradiation from inhalation and ingestion of material (including radon) from living on the landfill site in the future (residence)
* Although these people have the title of “workers” they are assessed as members of the public as they are considered to be unaware of the radioactivity present in the material they come into contact with.	

Each of the classes of workers described above are considered separate as they work in different parts of the process, hence no summing of these results over the different workers should be made. The doses presented are thus the total annual dose to any worker in that part of the industry indicated.

Doses to each class of worker (apart from transport) are given for three particle sizes. This is intended to represent the range of particle sizes of material that might be encountered in the industry. The doses to any particular worker can then be selected from those presented depending on the material to which the workers are exposed.

The highest predicted doses are about 2 mSv per year for raw material and fusion process workers. It must be noted, however, that some pessimistic and many general assumptions have been made to cover a wide variety of work tasks. Because of this, individual factories may not have workers who are exposed to doses of this magnitude. Also, good industrial hygiene and the wearing of facemasks or other protective measures will lower the inhaled component of the dose considerably. It is also noted that external irradiation is the dominant pathway for most of the workers considered, including those where the dose is above the level of 1 mSv per year. Control on access to storage areas, or the time spent in such areas where bulk material is kept, will decrease the total dose.

TABLE 2 The annual committed effective doses to workers associated with zircon sands

Group	Respirable details	Annual dose (Sv y^{-1})	Dominant pathway and % contribution
Transport	-	3.5 10^{-4}	External (100%)
Raw material process workers	1um particle size	2.1 10^{-3}	External (54%)
	5um particle size	1.9 10^{-3}	External (61%)
	10um particle size	1.4 10^{-3}	External (84%)
Fusion process workers	1um particle size	2.1 10^{-3}	External (54%)
	5um particle size	1.9 10^{-3}	External (61%)
	10um particle size	1.6 10^{-3}	External (70%)
Manufacturer workers	1um particle size	7.2 10^{-4}	External (62%)
	5um particle size	6.4 10^{-4}	External (70%)
	10um particle size	5.8 10^{-4}	External (76%)
Laundry workers	1um particle size	6.2 10^{-5}	Inhalation (99%)
	5um particle size	4.5 10^{-5}	Inhalation (99%)
	10um particle size	3.3 10^{-5}	Inhalation (98%)

Doses to members of the public from disposal of material

The predicted doses to members of the public from discharges and disposals from industries processing zircon sand are summarised in Table 3. This gives the annual dose to members of the public from the discharges from various stages of the industry, and also indicates the dominant pathway and its percentage contribution to the total dose. Doses from the normal use of the products are not included as they are considered to be well below those from disposal and discharges.

Two types of emissions to atmosphere were considered when calculating the doses to members of the public who live near to a factory. The first is the release of material from the fusion process (exposure to fusion off-dust). The second is the release of material from the site by fugitive emissions that includes, for example, loose material suspended and blown off the site by wind action (exposure to general processes). For liquid effluent, the doses from likely discharges to a local river of material from the chemical processing of zircon sands were considered; the doses from liquid effluents from other parts of the industry are much smaller than those given here due to the limited amount of material released. The doses from landfill disposal reflect those from the disposal of wastes arising from the fusing of zircon sands (fusion off-dust material) and from the chemical processing of zircon sands (general waste materials). It was considered that only fusion off-dust is sent to landfill in a form that could expose a worker. However, doses to members of the public are not affected by the disposal conditions so exposure has been considered to members of the public from the future use of the landfill site from both waste types. Exposure to future site users is from the excavation of the site for construction work and to residents living on the site in the future. It is considered that the other processes in the industry produce little or no waste when compared to these two processes and the doses from their disposals are not considered.

The peak dose from the release of material to atmosphere is 3.7 10^{-8} Sv per year, with the dominant pathway being the inhalation of material from the plume as it passes over local houses.

TABLE 3 Doses to members of the public from discharges and disposals from the zircon sands industries

Discharge or disposal route	Material description	Dose (Sv y^{-1})	Dominant pathway and % contribution
Atmospheric releases	General processes	1.1 10^{-8}	Plume inhalation (98%)
	Fusion off-dust	3.7 10^{-8}	Plume inhalation (96%)
Liquid effluent disposal	Chemical washings	1.6 10^{-10}	Canoeing, external (62%)
Landfill disposal	Future site users from general (wet) material disposal	7.5 10^{-4}	Resident, external (85%)
	Future site users from fusion off-dust disposal	4.5 10^{-6}	Resident, external (85%)
	Landfill workers (exposure to fusion off-dust only)	1.5 10^{-5}	External (98%)

The predicted doses from the disposal of material to local water systems is about 1.6 10^{-10} Sv y^{-1}, resulting mainly from external irradiation whilst in a canoe. The predicted doses from landfill disposal arise from the disposal of two material types: wet material from the chemical processing of zircon sand and the waste produced by the air filters in the fusion process. If the site is redeveloped in the future, doses of up to 0.75 mSv y^{-1} are estimated for a resident living on a site that had received general waste from the zircon sand industry. The doses from general material disposal is much larger than that calculated for the disposal of fusion off-dust mainly due to the amount of material being disposed (20,000 tonnes compared to 50 tonnes).

The dose to landfill workers is 1.5 10^{-5} Sv y^{-1}. This dose assumes that waste is sent to the landfill in a form that could readily expose workers, which is not the case for most of the waste sent to landfill from this industry. For most disposals from this industry the doses to landfill workers can be considered as trivial.

The doses from living in a house from radon inhalation, and the activity concentrations of radon in the home, are presented in Table 4. The results in this table assume that the activity concentration of ^{226}Ra (the parent of ^{222}Rn) remains about the same over the period between when the waste was disposed until housing has been constructed on the site. It is also assumed that a 1m layer of clean soil has been placed over any wastes disposed and that this remains in place after construction.

Table 4 Doses from radon inhalation in a house built on a disused landfill site and the activity concentration of the radon in the home

	Dose (Sv y^{-1})	Activity concentration (Bq m^{-3})
Radon inhalation - minimum	1.06 10^{-2}	2.1 10^{2}
Radon inhalation - maximum	1.69 10^{-2}	3.4 10^{2}

Two results are given in the table: these represent the range of doses and activity concentrations that may be present due to the methodology used. It is evident from the table that the range represents an activity above the action level of 200 Bq m^{-3}, so any new housing constructed on the site may have to have some features to reduce the radon level. However, the results are not conclusive as it has been assumed that radon is free to leave the disposed sand in a similar manner to that of soil (due to the availability of data). If the radon is trapped for the most part within the crystal structure of the zircon sand, as is currently believed to be the case, then the levels of radon released will be greatly reduced and hence the activity estimated above will also decrease. It has also been assumed that the house has been constructed entirely on an area above zircon waste. Given the relatively small amount of zircon waste disposed of compared to the volume of the landfill, this represents a pessimistic assumption.

Application of legislation to the industry in the UK

In the UK, the Ionising Radiations Regulations 1999 (SO, 1999) (IRR99) deals primarily with regulating the radiation exposures that people receive at work. Regulation 3 (Application) indicates that the IRR99 shall apply to “any work with any radioactive substance containing naturally occurring radionuclides”. In fact, the application of the IRR99 to such work depends on the definition of “radioactive substance”, as described in Regulation 2(1) and, more specifically, in paragraph 11 of the Approved Code of Practice (HSE, 2000). According to this, the IRR99 are deemed to apply to work activities where it is likely that persons could receive an effective dose in excess of 1 mSv per year. Where the IRR99 do apply, then appropriate controls are required to limit exposures. From the results presented in the report described here there is a strong indication that this legislation does apply to this industry. However each premises in the industry will require a site-specific assessment that takes into account features that are present rather than relying on general, industry-wide assumptions as used in the report. The application of the IRR99 is seen in some zircon processing premises where such site-specific assessments have indicated that the regulations do apply.

The Radioactive Substances Act 1993 (HMSO, 1993) (RSA93) regulates the holding of radioactive material, and the accumulation and disposal of radioactive waste, principally to control doses to members of the public. Under the provisions of the RSA93 all undertakings that use radioactive materials need to be registered and the accumulation and disposal of waste authorised, unless the material is excluded or exempted from the RSA93. The RSA93 applies to natural radioactivity; however, materials which have activity concentrations of naturally occurring radionuclides (other than those involved in the nuclear fuel cycle) lower than the values given in Schedule 1 of the RSA93 are not considered to be radioactive. These can therefore be excluded from the provisions of the Act. In addition to this exclusion, there are a number of Exemption Orders (EOs) made under the RSA93 that exempt specific materials from certain provisions of the RSA93.

The concentrations of radionuclides in zircon sands and in the wastes produced by the zircon sands processing industry in the UK are above the values presented in Schedule 1 of RSA93 for most radioelements. However, they are all below the values given in the Phosphatic Substances (Rare Earths, etc.) Exemption Order (HMSO, 1962). In certain processes, enhancement of some radionuclides may occur (although other radionuclide activity concentrations may decrease). The main example in the zircon sand industry is during the fusion of material where an enhancement of volatile elements in off-gases and dust could occur, with most of this material being collected in filters. However, using the source term for the report, no radioelements from either general or collected filter material exceed the limits of the EO. It is noted that the activity concentrations used in the report are conservative for zircon sands processed in the UK and the materials used in UK industry may have activity concentrations that are significantly lower than those presented here.

Summary

The results of a study to investigate the radiological consequences to the UK population of zircon sand operating plants within the UK are presented. The maximum dose to the workers involved in the processing of zircon sand, and in the manufacture of products from this material, is around 2 mSv per year. This is above the level at which the IRR99 requires an assessment to be carried out, and this could lead to the implementation of monitoring and control regimes to limit exposure. It is noted that such regimes are in place in zircon sand processing factories where site-specific assessments have shown that they are warranted. The maximum dose from the disposal of wastes from this industry is 15 μSv per year for exposure at the present time. This is to landfill workers where no controls over disposal are in place. However, controls are known to be in place for the disposal of most of the wastes generated by the industry so the dose to the majority of these workers is thought to be considerably below this level. Future exposure to waste sent to landfill could result in doses up to 0.75 mSv from someone living on the site after it has been developed. However, there is considerable uncertainty in this calculation so the possible dose could be significantly below this level. The predicted activity concentration of radon in houses constructed on a landfill that has received waste from the industry could be above the action limit of 200 Bq m^{-3}. This indicates that features may be required in any new houses built on the site to limit radon concentrations.

In order to put the above doses into context it is worth noting that the average annual dose to the UK population is of the order of 2.6 mSv y^{-1}, with a wide variation depending on the location (Hughes, 1999).

References

European Commission (1996). Council Directive 96/29/EURATOM of 13 May 1996 laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation, Official Journal of the European Communities, OJ L159 29/06/1996, p0001 - 0114.

European Commission (1999). *Establishment of reference levels for regulatory control of workplaces where materials are processed which contain enhanced levels of naturally-occurring radionuclides*. Radiation Protection 107, EC Luxembourg.

European Commission (2001). *Practical Use of the Concepts of Clearance and Exemption – Part II: Application of the Concepts of Exemption and Clearance to Natural Radiation Sources.* Radiation Protection 122 Part II, EC Luxembourg.

HMSO (1962). The Radioactive Substances (Phosphatic Substances, Rare Earths etc.) Exemption Order 1962, No. 2648.

HMSO (1993). The radioactive Substances Act 1993. ISBN 0 10 541293 7.

HSE (2000). *Work with ionising radiation Approved Code of Practice and guidance*. HMSO. ISBN 0 7176 1746 7.

Hughes, JS (1999). *Ionising radiation exposure of the UK population: 1999 review.* Chilton, NRPB-R311.

Oatway WB, Jones JA, Shaw PV and Mobbs SF. *Radiological Impact on the UK Population of Industries which Use or Produce Materials Containing Enhanced Levels of Naturally occurring Radionuclides: Part IV: Zircon Sands Industries*. NRPB. To be published.

SO (1999). The Ionising Radiations Regulations 1999. SI 1999/3232. ISBN 0 11 085614 7.