LEACHING OF RADIUM FROM MINE DEPOSITS – A POSSIBLE SOURCE OF GROUNDWATER CONTAMINATION

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1 ABSTRACT

Saline waters occurring in underground coalmines 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 unusual situation is observed in coalmines, 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 waste with technologically enhanced natural radioactivity (TENR) is a very important subject.
Mine waters can cause a severe impact on the natural environment, mainly due to its salinity. But also the enhancement of radium concentration in river waters, bottom sediments and vegetation is observed. Sometimes radium concentration in rivers exceeds 0.7 kBq/m^3, which is due to Polish law a permissible level for wastewaters. Mitigation measures have been applied in several coalmines. Therefore the total activity of radium, transported into rivers, is year by year smaller.
Lately another problem appeared – due to the decrease of the production of Polish coal industry and dismantling of several coalmines - 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, the leaching 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 quite important and significant for the further pollution of the adjacent areas of the settling ponds in the future.

2 ENHANCED NATURAL RADIOACTIVITY

The presence of natural radioactivity in uranium mines was known from early times. In other types of mines (such as for coal or phosphate) enhanced levels of natural radioactivity have been observed, but unfortunately this problem is not so well recognised.
The enhanced levels of gamma radiation in Polish coal mines were discovered in the early 60's [Saldan, 1965], and regular investigations were started in the 70's [Tomza & Lebecka, 1981]. These studies concentrated on radium-bearing waters and radioactive deposits. In one coalmine in Poland the radium concentration (^{226}Ra) in precipitate reached 400 kBq/kg, and this has the same activity as 3% U ore. Similar problems in the Ruhr Basin were reported by Gans [Gans et al., 1981], who also found high radium concentration in waste waters from coal mines. Natural radioactivity enhanced by effluents from phosphate industry has been investigated in Brazil [Paschoa & Nobrega, 1981]. Very high radium concentrations have been found in the USA in waste brines from the oil and gas industry [Maksimovic & Movrey, 1994]. As a result of radium precipitation from such waters in pipes etc. highly radioactive scales are formed. A similar situation has been observed in the Romanian oil industry [Sandor, 1995], which caused contamination of the natural environment.

The Upper Silesian Coal Basin (USCB) is located in the southern part of Poland and there are of about 50 underground coalmines. The total water outflow from these mines is about 800 000 m^3/day. The salinity of these brines if 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, and these waters 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].

Investigations, done by Tomza and Lebecka [Tomza & 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 coalmines [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 A 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 [Decree, 1989].

In the past the highest concentration of ^{226}Ra in discharge waters from a single coal mine in USCB was as high as 25 kBq/m^3 [Skubacz et al., 1990]. According to Polish regulations waters with radium ^{226}Ra concentration over 0.7 kBq/m^3 should be treated as waste with enhanced natural radioactivity [Decree, 1989]. Such waters were released from ten out of the sixtysix underground hard coal mines in Poland, in which radium-bearing waters were originally dumped via settlement ponds into the natural environment. Type A waters were originally discharged from seven coalmines (now three). The total activity of ^{226}Ra released with these waters is about 30 MBq per day. Although Type B waters were discharged from only three mines, the total output of ^{226}Ra is higher than for Type A waters - approximately 225 MBq per day [Lebecka et al., 1994]. The occurrence of enhanced natural radioactivity in Polish coalmines is a potential radiation hazard for mining crews. In the mining industry in Poland, monitoring of the radioactivity of mine waters and precipitates, as well as gamma doses, is obligatory since 1989. The monitoring system provides an opportunity to obtain a complete picture of the influence of an individual mine on the natural environment.

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 distances 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.

3 APPLIED METHODS AND INSTRUMENTATION.

A. Measurements of radium isotopes in waters

Radioactivity of waters from coalmines 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) and ^{224}Ra (LLD = 50 Bq/m^3).

B. Measurements of gamma emitting natural isotopes in solid samples

Solid samples (deposits from settlement ponds, river beds,soils, solid wastes, ashes) mainly contain radio-isotopes from the uranium and thorium decay series, ^{40}K and sometimes ^{137}Cs (from the Chernobyl disaster). For these measurements a gamma spectrometry system was used - it comprises an HPGe detector (45%, PGT), multichannel analyser connected with a computer (CANBERRA) and the GENIE-PC software for spectrum analysis (CANBERRA). This instrumentation enables measurements of ^{226}Ra concentration (as low as 1 Bq/kg), ^{228}Ra and ^{224}Ra, ^{40}K and other natural and artificial isotopes [Lebecka et al., 1996] on the similar levels.

4 THE SCOPE OF THE INVESTIGATIONS

Several different samples of bottom sediments were collected for further investigations – mainly bottom sediments from two big settling ponds, but also sediments from underground galleries and waste rocks were used. Results of gamma spectrometric measurements are shown in table 1.

Table 1. Concentration of natural radionuclides in chosen deposits [Bq/kg].

No.	Sampling place	Ra-226	Ra-228	Ra-224	K-40
1.	Bojszowy Reservoir, near outlet to Gostynka River –type B waters	344±18	413±18	408±30	530±67
2.	Bojszowy Reservoir, near inflow from Czeczott Colliery – type B waters	1844±110	4391±177	735±53	653±89
3.	Bojszowy Reservoir, near inflow from Piast Colliery – type B waters	442±21	1042±42	460±45	419±33
4.	Rontok Reservoir, bottom sediments – type A waters	8289±288	3177±55	2716±108	472±132
5.	Chwałowice Colliery, underground deposits – type A waters	35900±510	25200±390	20800±470	1790±365
6.	Piast Colliery, Waste rock from the surface disposal pile	83±6	74±3	70±6	724±87

It can be seen, that the span of radium content in samples of deposits is very large. Moreover, in different samples radium is present in a different chemical form. It should ensure the reliability of achieved results.

5 RESULTS OF INVESTIGATIONS

As mentioned above, at first gamma spectrometry was made for all chosen sample. Later the technique of investigations was as follows. 50 grams of dried sediment have been mixed with 0.5 l of distilled water. Admixtures of 5 grams of NaCl or 1 gram of K_2SO_4 or 0.5 g of $BaCl_2$ have been used to simulate the salinity, sulphate ions or barium ions presence in a groundwater. Such mixture was put onto the magnetic stirrer and stir continuously one hour. Later samples were left in the contact for a time period from few hours up to 7 days. After the sedimentation of the suspension, the water have been filtered and concentrations of ^{226}Ra and ^{228}Ra have been measured in the filtrate. The measurements have been done in a standard way with application of liquid scintillation counting, preceded by a chemical separation of radium isotopes with barium carrier [Chalupnik & Lebecka, 1993].

Fig.1. Re-enty of radium from bottom sediments samples 1 and 2 from Bojszowy Reservoir

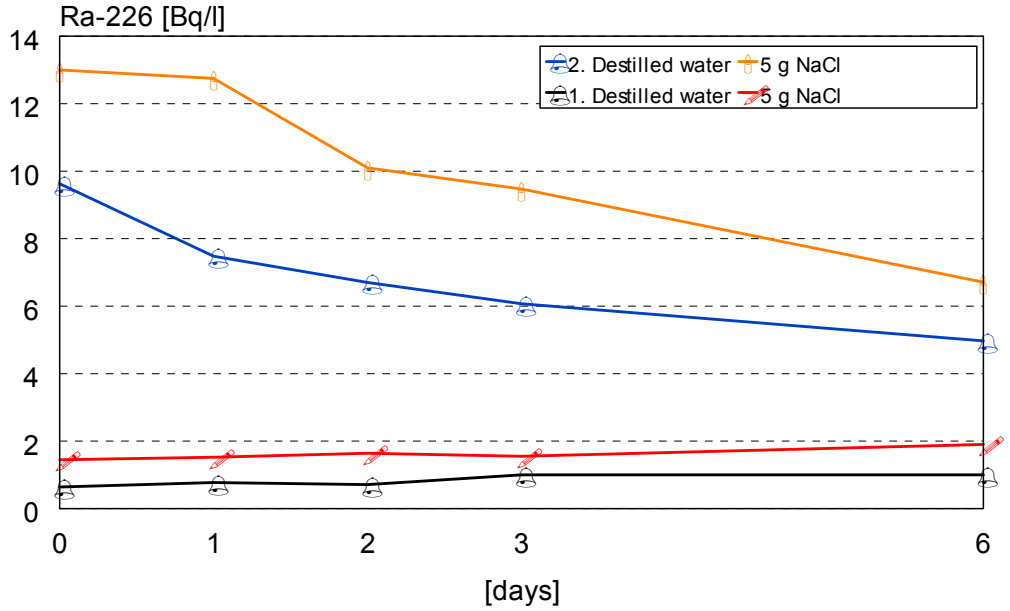
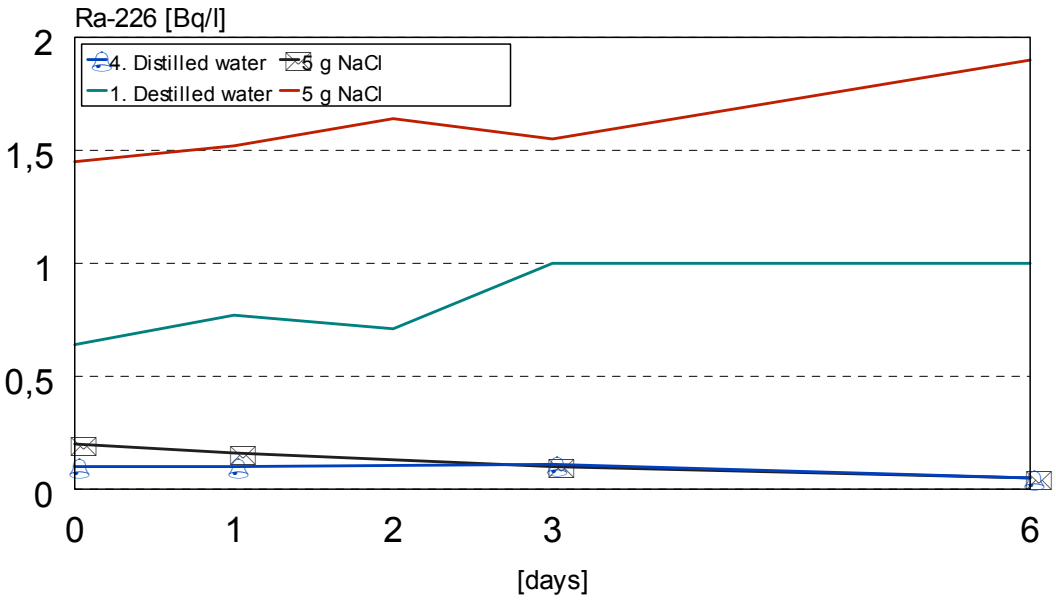


Fig.2. Comparison of the leachability of radium sample 1 from Bojszowy, sample 4 from Rontok



The first experiment was made for two samples from Bojszowy Reservoir and for one sample from Rontok Reservoir. Into Bojszowy settling pond type B waters (without barium) are discharged. Therefore radium is adsorbed on the surface of small grains of suspension but not precipitates out in a form of insoluble sulphates. We predicted that the re-entry factor should be significantly higher in comparison with that factor for deposits from type A waters. Such waters are dumped into Rontok settling pond. Results are shown in figures 1 and 2.

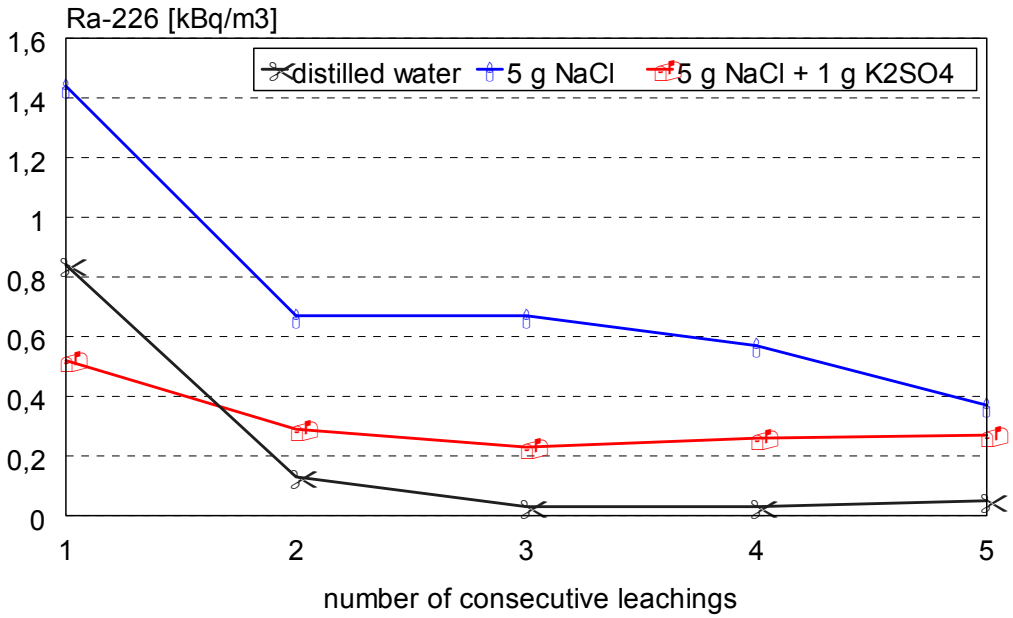
Preliminary results confirmed our prediction. For samples from Bojszowy Reservoir the salinity increased the leachability of radium isotopes from sediments. The re-entry factor for sample 1 was calculated as 5 % for ^{226}Ra and 4 % for ^{228}Ra. Similar results were found for sample 2 from the same settling pond. The re-entry factor was equal 7 % for ^{226}Ra and 5 % for ^{228}Ra. These results are in agreement with lately published results of American investigations, performed for soils with enhanced radium content in the area of oilfields [Rajaretnam & Spitz, 2000]. They found the re-entry factor of radium from the soil at the level 1.3%. In the contrary, for the sample no. 4 from Rontok Reservoir the re-entry factor for both radium isotopes was extremely low and not correlated with the salinity of the water. We found the re-entry factor as low as 0.004% for ^{226}Ra and 0.006 % for ^{228}Ra. In our opinion the reason is that radium in such sediments can be found in a form of insoluble radium sulphate, co-precipitated with barium sulphate. Our results for these sediments are in good agreement with chemical data of radium sulphate solubility [Chemical handbook, 1976].

On the other hand the radium concentration in water after experiments was often clearly enhanced in comparison with radium content in a typical groundwater - usually in groundwater radium content ^{226}Ra is not higher as 0.1 Bq/l [UNSCEAR, 1982]. This value is much lower than radium concentration in waters during our experiments, especially for sediments from Bojszowy settling pond. It seems to be the result of a different chemical form of radium, only adsorbed on the surface of grains of the deposits, settled on the bottom of the pond.

Another experiment was designed to check if radium from sediments can be washed out continuously with the same rate during long period of time. It seems to be important, because groundwater would stay in the contact with deposits, buried under the surface, for years. The deposit from Bojszowy reservoir (sample no. 3, table 1) was taken into investigations, because we predicted higher availability of radium from such sediments. 50 grams of the chosen sample was mixed with distilled water and left in the contact for 7 day. After this period the water was filtered and radium analysis have been done for the filtrate. But the sample was consecutively mixed with another portion of water. This procedure was repeated 5 times. Simultaneously, the same procedure has been done for another sample of deposit, but in the water 5 grams of NaCl (10 g/l) was dissolved. Exactly the same investigations were made for one more

sample, but in this case water contained not only NaCl but also 2 g/l of K_2SO_4. Results of these experiments are shown in figure 3.

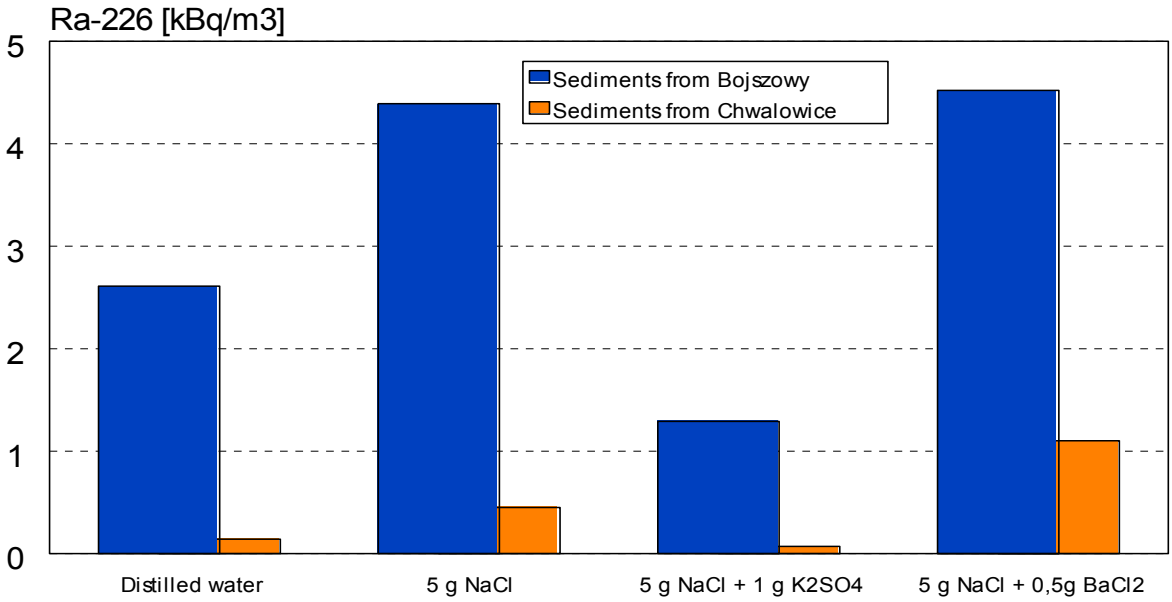
Fig.3. Consecutive leachabillity of radium from sediments



It can be clearly seen that the re-entry factor for radium is the highest in all cases for the first filtrate. For further experiments, under the same conditions, the radium content in the water decreases rather significantly, by factor 2 or even more. Rather surprisingly, results of 2nd and further leaching show rather stable radium content in the filtrate. Of course, there are different patterns for different mixtures. We decided to use the admixture of K_2SO_4 to slow down the leaching of radium from the sediment, due to the fact that radium sulphate is almost insoluble and the presence of such ions in the mixture should cause such effect. We found a big difference in re-entry of radium into distilled water and into water with K_2SO_4. During first experiment the radium content in distilled water was higher as in the water with sulphate ions. But after the second experiment the ratio was different – radium content in distilled water was lower in comparison with the content in another filtrate. Probably it means, that the salinity increases the re-entry of radium from the sediment and the presence of sulphate ions is not sufficient to prevent it. Results show also, that distilled water or water with very low salinity is not capable to wash out significant amounts of radium from such sediments. It leads to the conclusion, that before the ground reclamation of the areas of settling ponds the salinity of the water and especially groundwater should be somehow diminished.

During third series of experiments we would like to check the influence of sulphate ions and barium ions, present in the water, on the re-entry factor of radium. The presence of barium ions should increase the re-entry factor, while the presence of sulphate ions leads to the decrease of the leachability. We made these experiments for two different samples – for sediments from Bojszowy Reservoir (sample no. 2, table 1) and for sediments from underground water galleries in Chwalowice Colliery (sample no. 5, table 1). In both samples we found enhanced radium concentrations. In case of sample no. 2 ^{226}Ra content was about 1.8 kBq/kg, while in sample no. 5 the concentration of the same isotope was as high as 35.9 kBq/kg. The reason of such differences of the level of radium concentration is connected with the type of radium-bearing waters. In Chwalowice Colliery the sediments are formed in the chemical process of co-precipitation of radium and barium as sulphates. In Bojszowy only absorption on bottom sediments (silts, clays) takes place. Results of mentioned above experiments are shown in figure 4.

Fig.4. The influence of sulphate and barium ions on radium leachabilit

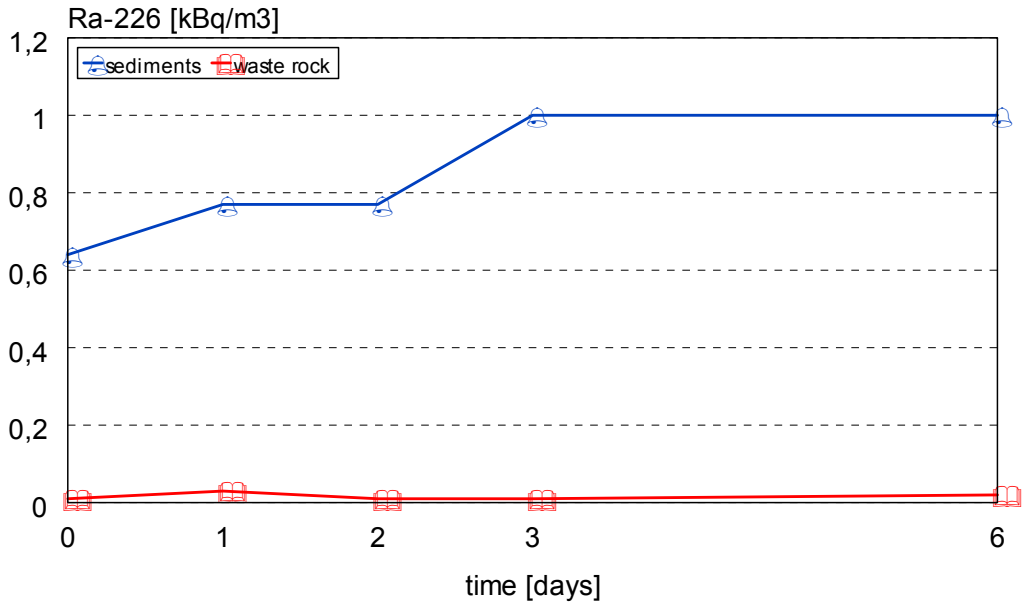


It can be clearly seen, that the availability of radium in different sediments varies a lot. Moreover, the presence of different ions in the water can affect the re-entry factor as well. First of all, sulphate ions in water could block the radium transfer from sediments into the water almost entirely - the similar effects we found in case of both type of sediments. Also the enhanced salinity of water leads to easier radium transfer from solid sediments into the water. On the other hand, the ratio of the re-entry factors into saline water to the re-entry factor into distilled water is bigger for sediments, which consist of radium and barium sulphate. It means, that in case of sediments with absorbed radium, water can easily wash out this isotope. For another type of sediments higher ionic strength

of saline water enables easier leaching of radium atoms, trapped in the lattice of barium sulphate crystals. Similar situation can be observed for the leaching of radium into the solution with barium ions – the presence of barium leads to the increase of radium entry factor, especially for deposits of radium and barium sulphates. Nonetheless, in all experiments radium concentration in the filtrate after leaching of radium from type B waters' deposits was higher as in filtrate after leaching from type A waters' deposits. The re-entry factor for deposits, formed from waters type A, is three orders of magnitude lower as the re-entry factor for deposits, settled from type B waters.

Finally we wanted to compare the leachability factors for bottom sediments and waste rocks from surface pile, sampled in the vicinity of one of coal mines. Our experiments were done for sediments from Bojszowy reservoir (sample no 1) and for rocks (mainly silts and shale), piled on the surface. The reason of such comparison is as follows. Large amounts of waste rocks have been dumped onto surface piles in the vicinity of coalmines. The radium content in such rocks is usually slightly higher as in the soil. The question was if the weathering of these rocks may cause the leaching of radium into groundwater. Results of these experiments are shown in figure 5.

Fig.5. Leachability of radium from botttom sediments and rocks



It can be seen, that the leaching of radium from waste rocks is negligible, especially in comparison with re-entry of radium into water from bottom sediments. We found in the filtrates from the experiments in which waste rocks were used, radium concentration at the levels close to values typical for groundwater in "normal" areas (below 0.1 kBq/m^3). It means, that the increase of the radiation hazard due to the contamination of groundwater can be

predicted only in the vicinity of settling ponds but not near the surface piles of waste rocks.

7 SUMMARY

The exploitation of coal may lead sometimes to the radioactive contamination of settling ponds of these collieries, where radium-bearing waters have been dumped onto the surface. It is a source of the radiation hazard for miners as well as for inhabitants of adjacent lands.
Nowadays, as a result of the closing of coal mines, on areas of settling ponds the ground reclamation must be done. It is difficult to predict the influence of large amounts of bottom sediments on groundwater contamination. The long-term stability of mine deposits with enhanced radium concentration seems to be an important factor, controlling such processes.
Preliminary investigations of the radium leachability from different types of bottom sediments, with different concentrations of radium isotopes have been done. It show, that the re-entry factors of radium from solid deposits into water depend on strongly the environmental conditions. On the other hand, leachability of radium may vary in a very wide range, accordingly to results of our investigations from $5*10^{-3}$% up to 10%.

In my opinion preliminary results are very interesting and such investigations must be carried out in the future. The half life of ^{226}Ra is 1620 years and traces of radioactive contamination will be lasting centuries after the end of underground exploitation in different coal basins.

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