

PROBLEMS WITH ACTIVITY DETERMINATION IN NATURALLY OCCURRING RADIOACTIVE MATERIALS

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Abstract

Materials resulting from decommissioning of plants for natural oil/gas extraction, in mining industry, fertilizer and aluminium production and ground water extraction are often contaminated with radionuclides of natural origin. Activity of materials with natural radioactivity is usually determined by γ -spectrometry. To simplify this measurement, radionuclides of the natural decay chain are considered in balance. However, due to chemical processes, the natural nuclide vectors may vary significantly. They range from the radium isotopes to the complete uranium or thorium decay chain. A change of the $^{234}\text{U} / ^{238}\text{U}$ ratio was also found. During further processing (such as melting) of this kind of material, the nuclide vector may split even further, resulting in further enrichment of individual nuclides in the waste. If nuclide determination is problematic, other measurement techniques than γ -spectrometry should be applied.

Material origin

Siempelkamp Nuklear- und Umwelttechnik (SNU) GmbH & Co. has long-time experience in the recycling of metallic scrap from the nuclear industry. Up to now, approx. 10,000 Mg were melted and recycled for the production of cast components for the nuclear industry. Due to the increased



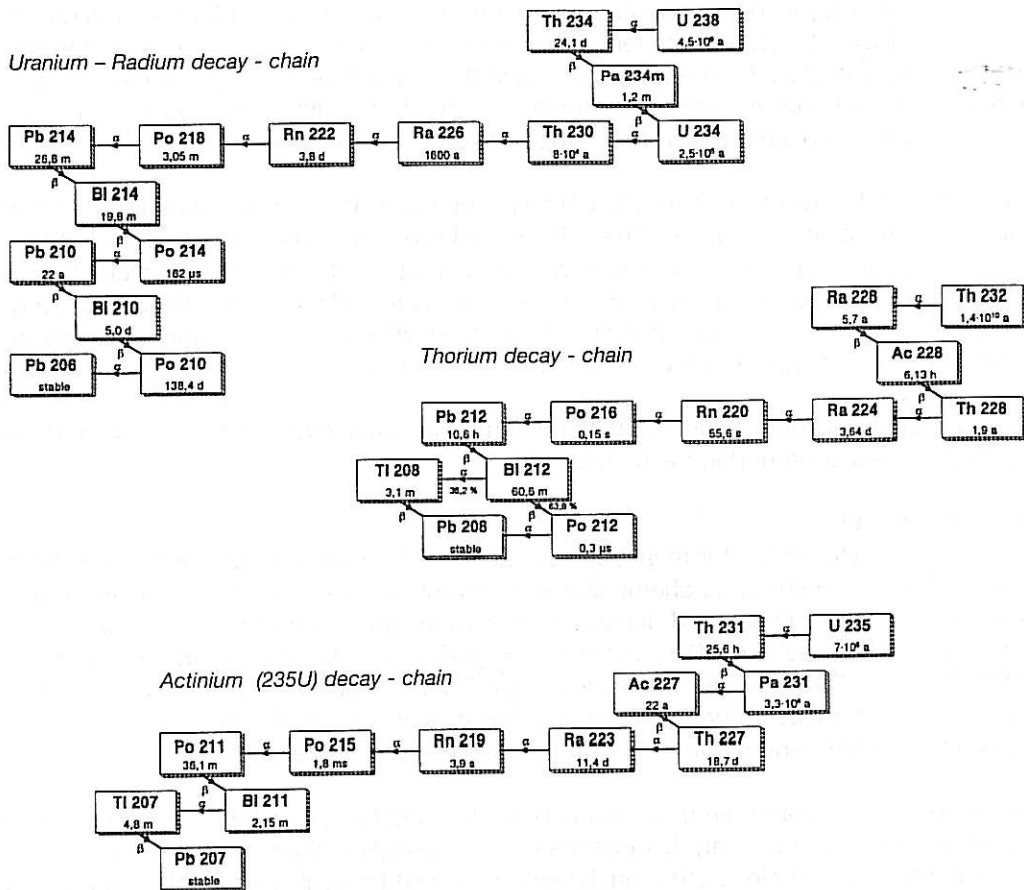
Fig. 1: Example of NORM-Material

demand for recycling of chemically contaminated steel scrap, a new facility was built at Siempelkamp site. There is processed metallic scrap from dismantling of plants of the petroleum-, natural gas- and mining industry (fig. 1) as well as the chemical industry. Processing of materials originating from the groundwater - and swamp water advancement is also planned. In the development stage, approx. 800 Mg of steel scrap were successfully decontaminated [5].

These materials are usually contaminated with naturally occurring radionuclides like the primordial radionuclides, which emerged at the origin of the earth and have longterm half-lives as well as their more short-lived decay products, which are formed constantly new.

Primordial radionuclides

The most important primordial radionuclides are ^{238}U , ^{235}U , ^{232}Th and ^{40}K . The nuclide ^{238}U is the mother nuclide of the uranium - radium - decay chain as well as ^{235}U of the uranium - actinium - chain. The mass concentration of ^{235}U in the natural uranium is 0,72 %. ^{232}Th is the mother nuclide of the thorium - decay - chain, which contains isotopes of the same elements as they occur in the uranium - radium - chain. The activity of ^{40}K in natural potassium is about 30 Bq/g, e.g. 0,6 Bq/g in soil.



Deviations from equilibrium state

In deposit sites of uranium respectively thorium, the mothernuclides are usually in radiological equilibrium with their daughters. This is based on the very long half-lives of the mother-nuclides in comparison to that of their daughters. In this case, all radionuclides of one decay chain have the same activity. For natural uranium, the ratio of $^{238}\text{U} : ^{234}\text{U} : ^{235}\text{U}$ is about 1:1: 0,05. If equilibrium state can be stipulated, determination of activity of the whole decay chain is quite easy, by means of only one gamma-emitting nuclide, e.g. $^{234\text{m}}\text{Pa}$ for the uranium decay chain. Because of their different geochemical behavior, a deviation from equilibrium state is quite frequent. For measurements and the following activity-calculation it is recommendable to use subgroups of the main decay chains (Table 1).

Table 1: subgroups of natural decay-series

(Bold-face nuclid names: easy to measure with gamma spectrometry.
Underlined nuclid names: measureable with gamma spectrometry.)

uranium-radium-series

- I. $^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234\text{m}}\text{Pa} \rightarrow ^{234}\text{U}$
- II. ^{230}Th
- III. ^{226}Ra
- IV. $^{222}\text{Rn} \rightarrow ^{218}\text{Po} \rightarrow ^{214}\text{Pb} \rightarrow ^{214}\text{Bi} \rightarrow ^{214}\text{Po}$
- V. $^{210}\text{Pb} \rightarrow ^{210}\text{Bi} \rightarrow ^{210}\text{Po} \rightarrow ^{206}\text{Pb}_{(\text{stable})}$

uranium-actinium-series

- I. $^{235}\text{U} \rightarrow ^{231}\text{Th}$
- II. ^{231}Pa
- III. $^{227}\text{Ac} \rightarrow ^{227}\text{Th} \rightarrow ^{223}\text{Ra} \rightarrow ^{219}\text{Rn} \rightarrow ^{215}\text{Po} \rightarrow ^{211}\text{Pb} \rightarrow ^{211}\text{Bi} \rightarrow ^{207}\text{Tl} \rightarrow ^{207}\text{Pb}_{(\text{stable})}$

thorium-series

- I. ^{232}Th
- II. $^{228}\text{Ra} \rightarrow ^{228}\text{Ac}$
- III. $^{228}\text{Th} \rightarrow ^{224}\text{Ra} \rightarrow ^{220}\text{Rn} \rightarrow ^{216}\text{Po} \rightarrow ^{212}\text{Pb} \rightarrow ^{212}\text{Bi} \rightarrow ^{212}\text{Po} / ^{208}\text{Tl} \rightarrow ^{208}\text{Pb}_{(\text{stable})}$

Each individual subgroup is determined by one gamma-emitting nuclid, e.g for the uranium radium series ^{234m}Pa or ^{214}Pb / ^{214}Bi . Due to the long half-lives of the first members of each subgroup, one can find an equilibrium state for these subgroups in the geosphere. Specially in the hydrosphere, disturbances of the equilibrium state are often found, due to the different solubility of the radionuclids. This could be observed even for isotopes of the same element.

Water in contact with uranium-containing rocks is enriched with ^{234}U , caused by the recoil effect of nuclear transformation by α -decay. The ^{234}Th daughter of ^{238}U at the rocks surface left the matrix because of its high kinetic recoil energy and thus passes to the liquid medium. In samples of storage-, drink- or groundwater, the activity-ratio of ^{238}U to ^{234}U was determined to 1:1,2 up to 1:1,5. A ratio up to 1:10 has been measured in some isolated cases. In contrast to this the activity-ratio of ^{238}U : ^{235}U was not changed and still is 21,7:1 [3].

Because of its limited solubility, thorium is hardly found in water. Only ^{228}Ra and ^{224}Ra and their short-lived daughters are found in fresh water.

Measuring of activity

A method, which is quite simple for measuring the activity of specific radionuclides is gamma-spectrometry. For this method, no chemical preprocessing is necessary before measurement. Only geometrical characteristics and density of the sample are important for determination of the activity. Siempelkamp uses two HPGe-detectors (High-Purity Germanium) 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 ^{210}Pb at 46.5 keV with sufficient efficiency.

However, there may be more than one nuclide present in the sample within a specific gamma-energy-area. In this case, the analysis depends on the energy-resolution of the detector. If the activity determination is not clear, other nuclid energies must be evaluated. Table 2 shows some examples.

Tab. 2: nuclide energies in the same area

radionuclides	decay-series	gamma-energies [keV]
^{212}Pb ; ^{214}Bi	thorium ; uranium-radium	74.8 ; 76.5
^{231}Th ; ^{228}Th	actinium ; thorium	84.2 ; 84.4
^{226}Ra ; ^{235}U	uranium-radium ; actinium	186.1 ; 185.7
^{224}Ra ; ^{214}Pb	thorium ; uranium-radium	241.0 ; 241.9

If the activity-measurement with a gammaspectrometrical installation is not sufficient, other methods are necessary for determination, such as radiochemical analysis or alpha- or beta spectroscopy.

Determination of activity

After measuring the activity of all measurable radionuclides, the activity relevant for transport and acceptance has to be calculated. There are different ways for calculation, which are shown in table 3 below. In the first two cases the activities of all radionuclides of the uranium- and the thorium-decay chain, beginning with radium, are added up. In comparison to this, in the two last cases only the activities of nuclides with long half-lives ($T_{1/2} > 100$ d) are added up (acc. to StrlSchV [1]).

Tab. 4 shows an example for measured nuclid specific activity in quite fresh material. Obviously there was only ^{226}Ra separated in the mud. The subgroups III and IV of uranium-radium-series are in equilibrium. ^{210}Pb with a half-life of 22 years has not yet been reproduced in the same quantity.

Distribution of activity after melting

Chemical separation of the radionuclids incorporated in the materials is rather complicated, if at all possible. Therefore the material is melted, leading to a further enrichment of the radio-nuclides in melt, slag or dust.

Tab. 3: example of methods for activity calculation of material from oil/gas extraction industry [5] (old material)

method	calculation
physically	$a_{total} = (a_{Ra226} + a_{Rn222} + \dots + a_{Po210}) + (a_{Ra228} + a_{Ac228} + \dots + a_{Po212})$
Netherland	$a_{total} = 6 \cdot a_{Ra226} + 3 \cdot a_{Pb210} + 2 \cdot a_{Ra228 (Ac228)} + 7 \cdot a_{Th228}$
PTB, BEB, ADR	$a_{total} = a_{Ra226} + a_{Pb210} + a_{Po210} + a_{Ra228} + a_{Th228}$
Siempelkamp	$a_{total} = a_{Ra226} + 2 \cdot a_{Pb210} + 3 \cdot a_{Ra228 (Ac228)}$ In this case, ^{232}Th , which can not be detected by γ -spectrometry, is added to the total activity via the measured ^{228}Ac value, if the presence of ^{232}Th can not be definitely excluded

Tab. 4: example of measured activity in dry rests of mud in two drainage tubings.

nuclide	I [Bq/g]	II [Bq/g]
^{226}Ra	21	65
^{214}Pb	17	54
^{214}Bi	22	64
^{210}Pb	0,82	-

The measureable activity in the cast ingots is significantly below 1 Bq/g. ^{226}Ra resp. ^{228}Ra and some of their daughters are found mainly in the slag. The same is valid for uranium and thorium if they are present in the incoming material. Due to the casting temperature of about 1300 to 1400 °C, the nuclide ^{210}Pb does not remain in the melt. It passes the exhaust system and is collected and deposited in the dust. Table 5 shows the distribution of radionuclides of natural origin as it was found up to now.

Tab. 5: activity distribution after melting

nuclid	melt	slag	dust
$^{238}\text{U}, ^{235}\text{U}$	1%	98%	1%
$^{232}\text{Th}, ^{234}\text{Th}$	< 1%	> 98%	1%
$^{226}\text{Ra}, ^{228}\text{Ra}$	-	98	2
^{210}Pb	-	7	93

The effect of distribution of radionuclides in different waste fractions is shown in the figure 3 below. It is obvious, that most of the natural activity of the radium-series is transferred into the slag. But there is no energy-peak at 46.5 keV, that means no ^{210}Pb is found in the slag.

Opposite to this, the figure 4 shows only little energy-peaks for the natural activity in the dust. These are slight remainders of ^{226}Ra and some of its daughters. But now there is a very high peak at 46.5 keV. All of the activity of ^{210}Pb was concentrated in the filterdust. this is, due to the fact the lead will evaporate at normal melting temperatures above 1300°C.

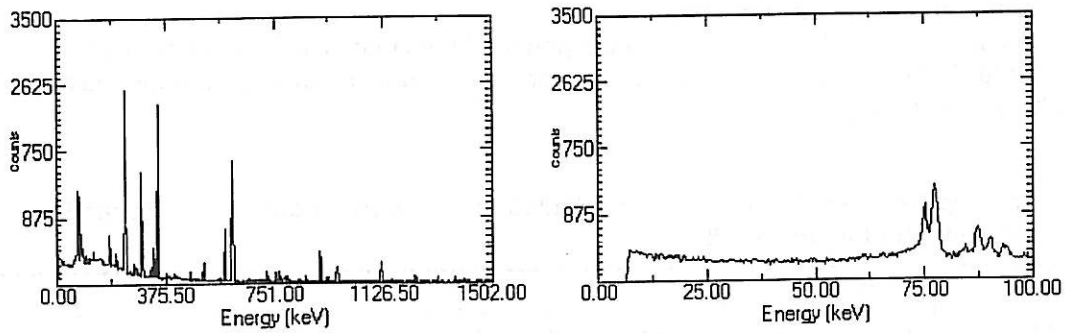


Fig. 3 : energy spectrum of radioactive nuclides in the slag after melting.
 Left fig.: energy peaks of thorium- and radium-decay chain.
 Right fig.: area around 46.5 keV, no ^{210}Pb

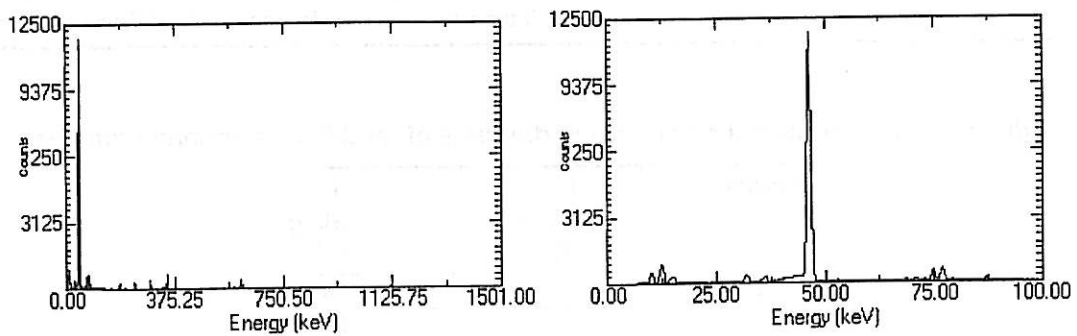


Fig. 4 : energy spectrum of radioactive nuclides in the filterdust after melting.
 Left fig.: whole spectrum, main peak is ^{210}Pb .
 Right fig.: area with energy peak of ^{210}Pb at 46.5 keV

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