INSTRUMENTAL AND RADIOCHEMICAL DETERMINATION OF NATURAL RADIONUCLIDES IN RAW AND WASTE MATERIALS

S. Niese, M. Koehler, B. Gleisberg,
VKTA Rossendorf, P.P. Box 510110, 01413 Dresden, Germany
E-mail: S.Niese@vkta-rossendorf.de

Introduction

We will present experiences in the determination of radionuclides of the Th and U decay series in raw and waste materials, the specific activity of the other natural radionuclides are too low for radiological importance. ^{232}Th, ^{235}U and ^{238}U have half-lives of the order of the age of the solar system have been formed by nucleosynthesis at extremely high temperatures in white dwarfs. The mean concentration in the solid solar matter (represented by the primary meteorites) amounts to 0.051 ppm Th and 0.014 ppm U, respectively /1/. During the development of the Earth both elements were enriched together with other large ion lithophile elements (LILE) in the Earth upper crust by a factor of about 200, reaching 10.5 ppm Th and 2.5 ppm U, respectively, corresponding to 42 and 31 Bq/kg ^{232}Th and ^{238}U Their electrochemical potential is too negative for the formation of metal alloys in the Earth's core and the radii of the ions are too large for cocrystallization with dense magnesium and iron silicates which form the Earth's mantle and lower crust. Fractionated crystallisation of magmatic melts, wheathering of rocks, dissolution in water, and absorption on minerals and organic matter yield a pattern of the distribution of Th and U from extremely low concentrations to highly concentrated ores. The geochemical distribution of the radioelements is the basis of the radiological investigation of materials containing natural radioactivity.

Methods for the determination of radionuclides

For the determination of K, Th and U a number of conventional chemical analytical methods as well as x-ray fluorescence spectrometry and spectrometry of the nuclear radiation are used. In the past we have mostly used neutron activation analysis for the investigation of the geochemical distribution of Th and U in rocks, minerals and sediments.

After the shutdown of the Rossendorf Research Reactor, we have determined the daughter nuclides of Th and U by gamma spectrometry. In water samples we enrich ^{210}Pb and ^{226}Ra by barium sulfate precipitation; in low activity samples ^{226}Ra is determined by measurement of the alpha rays of the emanated ^{222}Rn. Low activities of the isotopes of uranium, thorium and polonium in the decay chains are determined after chemical separation by alpha spectrometry. ^{227}Ac is determined by measurement of the daughter ^{227}Th after after attainment of radioactive equilibrium,either by gamma spectrometry or by alpha spectroscopy following chemical separation. The measurement of low radioactivity is carried out in an underground laboratory, where a 47m rock cover shields 98% of the cosmic muons and the neutrons produced by the muons in lead shields /2/. In a counting chamber shielded by about 25 cm of iron equivalent the gamma radiation from the natural radioactivity of the rock is reduced by three orders of magnitude and the detectors thereselves are shielded by additional 10 to 17 cm lead. The choosen counting conditions guaranteed that the relative standard deviation of the determinations did not exceeded 20 %.

Natural radioactivity in Saxonian tertiary volcanos /3/ and copper schist from the South of the Harz mountains /4/, as examples for geological materials

We have investigated the reason for the relatively high concentration of Th and U in phonolites. Saxonian tertiary volcanos are formed from mantle melts which are enriched with fluids containing elements with large ions e.g. alkali metals, Th and U. This enriched mantle is the reason for the uranium province in Saxonia, northern Bohemia, and Eastern Thuringia. As a result of the magmatic fractionation, the concentration of thorium and uranium in the phonolites are enhanced by a factor four in comparison with the neighbouring alkali basalts (Tab. 1). In the South of the Harz mountains we investigated the copper schist. Wheathering followed by absorption on organic matter caused the high concentrations of metals in this type of black schist (Tab. 2).

Table 1: Specific activities of ^{232}Th and ^{238}U in Lusatian alkaline rocks

Rock type	Location	Bq/kg ^{232}Th	Bq/kg ^{238}U
Phonolite	Johnsberg	164	172
Phonolite	Hochwald	175	143
Alkaline basalt	Mean value	39	27

Table 2: Specific activity of ^{232}Th and ^{238}U Bq/kg in copper schist /4/ in comparison with similar rocks

Nuclide	Range for copper shist	Mean value for black shist	Mean value for clay shist
^{232}Th	36 - 68	44	40
^{238}U	87 -8300	285	37

In comparison with the neighbouring clay layers the uranium in the brown coal in Lusatia is enriched by a factor 3. It was interesting, that we have found in the brown coal radioactive disequilibrium between ^{238}U and ^{226}Ra, the loss of radium beeing caused by its transportation with groundwater.

Radioactive disequilibrium in river sediments

The equilibrium of the nuclides of the decay chains in sediments in contact with water may be disturbed. We have measured samples of grain fraction smaller than 60 micro meters from the river Weisse Elster and some of its tributaries. The results are given in Table 3. The radionuclides at the source region (samples 1 and 2) of the Weisse Elster are nearly in radioactive equilibrium. The origin of the Culmitsch river is a tailings pond of a former uranium ore processing unit and this explains the excess of radium in sample No. 5. The relatively low activity of ^{210}Pb is a result of the sediment structure. During chemical processing the radium was coprecipitated with barium on the surface of the quartz grains. The radon may easily escape from the sediment and therefore we measured a deficit of ^{210}Pb. This can be observed also in the Elster river (samples 8 – 10). The origin of the water of the Wipsebach and the Gessenbach are mainly uranium mines and stockpiles. Weathering of pyrite produces sulfuric acid which mobilises the uranium from the stockpiles. In these two rivers we observe therefore an excess of uranium. Leaving the region of uranium mining, the radioactivity of the sediments decreases.

Table 3: Specific activity a(^{238}U) in Bq/kg and activity ratios in sediments of the Weisse Elster river and some tributaries. Sampling points ordered from the source to the mouth.

Sample No.	River	Location	a(^{238}U) [Bq/kg]	a(^{226}Ra) / a(^{238}U)	a(^{210}Pb) / a(^{226}Ra)
1	Weisse Elster	Bad Elster	115	1.4	1.0
2	Weisse Elster	Plauen	75	1.4	1.2
3	Gölzsch		340	1.1	1.2
4	Weisse Elster	Mouth of Gölzsch	180	0.53	1.2
5	Culmitzsch Pöltzschbach		3750	3.6	0.17
6	Wipsebach		2360	0.22	0.43
7	Gessenbach		3490	0.30	0.87
8	Weisse Elster	Gera	1050	0.47	0.17
9	Weisse Elster	Bad Köstritz	2050	0.28	0.55
10	Weisse Elster	Leipzig	506	0.51	0.66

Measurement of scratched samples from contaminated steel
Table 4 gives mean values of the radioactivity concentration of the layers of metal scratched from scrap steel measured by gamma spectrometry. Results of a sample with high contamination from a mine are shown in table 5. The chemical processes used during the mining e.g. washing of the equipment with recycled water, disturbs the radioactive equilibrium. Uranium and radium are well absorbed on the corrosion product layer while thorium and lead are washed out. The emanation of ^{222}Rn during the storage of the samples reduces the activity of ^{214}Pb and the emanation before sampling reduces the activity of ^{210}Pb.

In samples from uranium processing equipment ^{230}Th and ^{210}Pb were also reduced in comparison with ^{238}U. The mean values of the surface activity of ^{238}U in the scrap metal of the mines and the hydrometallurgical processes amounts to 0.45 Bq/cm^2 and 0.83 Bq/cm^2, respectively. High activities of radium were found only in equipment in contact with waste streams. Table 6 shows activity of the scratched layers of equipment used for hydrometallurgical processing.

Table 4: Arithmetic mean of the specific surface activity a(surface) in Bq/cm^2 of steel samples from mining and hydrochemical processing equipments

Process	Number of samples	^{238}U	^{226}Ra	^{210}Pb
Mining	77	0.18	0.18	0.06
Chemical processing	42	8	0.5	<0.3

Table 5: Surface activity a in Bq/cm^2 obtained by measuring of the scratched sample of a highly contaminated steel surface

Nuclide	a
^{238}U	2.0
^{230}Th	0.54
^{226}Ra	2.0
^{214}Pb	0.77
^{210}Pb	0.21
^{227}Ac	0.055

Table 6: Specific surface activity of ^{238}U in Bq/cm^2 of parts of equipments for the hydrometallurgical process with uranium contamination >4 Bq/cm^2

Sample	Surface activity Bq/cm^2	Activity concentration in the process solution Bq/l	Equipment
C2u	108	30	Tubes for concentrated solution
C1u	42	225000	Evaporator of the product
S2u	5.0	50	Inlet of the ore

A comparison of the specific activity of the scrubbed layer expressed as surface activity a_S with the surface alpha activity a_O measured with an instrument for detection of alpha contamination (measured area 150 cm^2, measured geometry 40) is given in table 8. The calculated surface activity a_S is higher than the measured surface activity. The ratio $F_{SA} = a_O / a_S$ is a self absorption factor depending on the activity covered by a material layer thicker than the range of the alpha radiation.

Table 7: Comparison of the measured surface alpha activity of a_O with an apparent surface activity calculated from the activity of the material scrapped off a_S in Bq/cm^2, d = thickness of the scrubbed layer in g/cm^2

Sample	a_S	a_O	a_O/a_S	d	(a_O/a_S) *d
CR03	0.50	0.15	0.30	0.043	0.013
CR04	0.81	0.5	0.63	0.007	0.004
CR05	0.33	0.1	0.30	0.011	0.003
CR06	1.67	0.55	0.33	0.035	0.012

The sample CR04 was relatively smooth and the scratched layer had a low mass. The low depth of nuclide penetration allows in this case an efficient measurement of the surface activity by direct measurement. The thicknesses of the scratched masses are not identical with the depths of the contaminated layer. Therefore the product (a_O/a_S) *d cannot be constant.

For calculation of the specific activity of the waste from remelting of the contaminated steel we assume a mean value of the thickness of the contaminated steel of 5 mm and assume that both sides of the metal sheets are contaminated, the equivalent thickness amounts to 2.1 g/cm^2, yielding a mean specific activity of the whole mass of the contaminated metal a(metal), Bq/g

a(metal),Bq/g = a(layer),Bq/cm^2 : 2.1 g/cm^2,

Table 8: Calculated specific activities in the scrap metal and in the waste in Bq/kg

Source of scrap metal	n	Metal		Waste	
		^{238}U	^{226}Ra	^{238}U	^{226}Ra
Mining	5	84	100	1700	2000
Hydrometallurgy	3	3600	230	72000	4700

Assuming that the necessary mass of the added mixture of chalk and fluorite amounts to about 5% of the steel and because of the fact that all natural radionuclides during the melting process are collected in the waste the specific activity of the waste amounts to
a(waste) = a(metal) * 20.
The remelted steel can be used without any restriction.

Gamma spectrometry of contaminated lead

For detector shields we need lead with an extremely low content of ^{210}Pb, especially for inner layers. When testing lead quality we have measured samples in relation to a sample certified by the PTB Brunswik.

After decommissioning of hot radiochemical laboratories, for large quantities of lead the level of contamination has been measured. Some of the material shows surface contamination too high for nonrestricted use, even after decontamination and remelting. Table 9 shows some measured nuclides in three remelted samples. We have demonstrated that the measured apparent surface contamination was caused by a high content of ^{210}Pb and the daughter ^{210}Bi /5/. In sample no. 3 we also observed the low gamma transition at 803 keV from ^{210}Po.

Table 9: Specific radioactivities in remelted lead from a hot laboratory in Bq/kg

Sample	^{210}Pb	^{226}Ra	^{214}Bi	^{40}K	^{60}Co	^{137}Cs
1	505	<10	<0.2	<0.2	<0.3	<0.1
2	495	<10	<0.2	<0.2	0.16	<0.1
3	13500	<80	<0.4	<0.2	<0.3	<0.1

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