Chemical types of bonding of natural radionuclides in technologically enhanced naturally occurring radioactive materials (TENORM)

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Abstract. TENORM (technologically enhanced naturally occurring radioactive material) is the acronym for solid material containing man-made elevated concentrations of naturally occurring radioactive elements. In this study, an enhancement is given if at least one radionuclide exceeds 200 Bq/kg. Raw materials, wastes and products were taken from the following types of industry: aluminium production, refractory industry, fertilizer production, hard coal mining and crude oil exploitation as well as Th-contaminated soils. In order to estimate their environmental hazard dimensions, the availability and mobilization potential of the natural radionuclides stored in those materials were investigated. For this purpose, the 3-step extraction procedure proposed by the European Bureau Communautaire de Référence (BCR) was applied as well as the German extraction procedures DIN 19730 and 38414-S4. The reagents obtained represent the water soluble, easily exchangeable, plant available, reducible and oxidizable level. These extraction solutions were then measured by gamma spectrometry for determining the activity concentrations of the following radionuclides: ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{228}Th. By doing so, the chemical types of bonding of these radionuclides can be evaluated. The measuring geometry for gamma spectrometry strongly depends on the reagent volumes resulting from the extraction procedures, which are about 200 mL. Therefore, a special calibration was introduced by using reference water of known radionuclide content from the German Federal Office for Radiation Protection (BfS). In order to verify the reliability of that calibration standard containing low, medium and high activity concentrations, a measurement comparison was undertaken in a second, independent laboratory, which confirmed the results. The described analytical procedures provide information about potential migration pathways of the natural radionuclides contained in TENORM as well as the radiological risks for workers dealing with TENORM and members of the public who may be affected (e.g. by dump sites, secondary use as building material).

1. Introduction

Within the framework of the EU project TENORMHARM, carried out from 1 November 2001 to 31 December 2004 under Contract No. FIGM-CT-2001-00174, TENORM samples were delivered from a Romanian aluminium production plant and a Belgian fertilizer industry. In Germany, solids were provided by a refractory production plant and crude oil exploitation company, sediments were taken from river banks affected by pit waters from hard coal mining and some soils contaminated especially by ^{232}Th progeny. The analyses of those materials by the three extraction procedures (BCR, DIN 19730 and DIN 38414-S4) and the determination of the reagents' activity concentrations were undertaken in the Geology laboratory of the University Duisburg-Essen.

2. Investigation methods

All the sample materials were dried for 24 h at 105°C and then homogenized by sieving for the grain size fraction <2 mm. An aliquot was separated from that to be measured by gamma spectrometry for its initial radionuclide content. Then, the amounts needed for each of the three extraction procedures were weighed precisely and transferred to acid-cleaned 250 mL propylene (PP) centrifugal cups. By the (successive) adding of several reagents, the radionuclides of different types of bonding were dissolved in those liquids. For the preparation of the chemical solutions needed, always bi-distilled water and chemical solutions of the purification degree 'p.a.' were used. All three procedures require extraction shaking, which was done by an overhead-shaker at 50 rpm in accordance with the time limits mentioned in the respective standard instruction. After each step, the suspension in the PP cup was centrifuged at 4500 rpm for 5 min; in some cases the centrifuging time was extended to 20 min if the suspension was not fixed on the bottom of the cup before. The separated extraction liquid was then decanted by a 45 µm membrane filter and transferred into an acid cleaned polyethylene (PE) storage cup of 250 mL volume. In terms of the sequential BCR procedure, the reagent of the next step was filled in the same PP cup, which contained the remaining solid material on the bottom from the extraction step before.

2.1. Extraction procedures

The three extraction procedures applied require different amounts of starting materials and different handling schemes, as shown in Table 1. The sequential extraction as proposed by the BCR was carried out according to [1], the references for those DIN procedures are Refs [2, 3] as given by the German Institute of Standardization.

TABLE 1. THE THREE EXTRACTION PROCEDURES APPLIED

Fraction	Procedure
BCR (starting material volume 5 g)	
F1 (easily exchangeable)	200 mL of 0.11 mol/L CH_3COOH, shaking time 16 h
F2 (reducible)	200 mL of 0.1 mol/L H_3NOHCl, pH 2, shaking time 16 h
F3 (oxidizable)	a) 2 × 50 mL 35 % H_2O_2, each heated up to near dryness b) 250 mL of 1 mol/L CH_3COONH_4, pH 2, 16 h shaking time
DIN 19730 (starting material volume: 80 g)	
F4 (plant available)	200 mL of 1 mol/L NH_4NO_3, shaking time 2 h
DIN 38414-S4 (starting material volume: 20 g)	
F5 (water soluble)	200 mL of bi-distilled H_2O, shaking time 24 h

In summary, five liquid fractions were obtained as representatives of the easily exchangeable (F1), reducible (F2), oxidizable (F3), plant available (F4) and water soluble (F5) level.

2.2. Gamma spectrometry

The setup of the high resolution gamma spectrometry method comprises an n-type HPGe detector of quasi-coaxial shape, equipped additionally with a beryllium window for including also gamma energies lower than 100 keV. This system is controlled by InterWinner 5.0 software made by ORTEC and calibrated with GENITRON standards in different volumes for the relevant radionuclides of the ^{238}U decay series (Series-Nr. 92-M-134) and ^{232}Th decay series (Series-Nr. 92-M-112). The radionuclide detection procedures as presented in Table 2 require radon-dense measuring boxes to allow radioactive equilibrium to be established, therefore the boxes were sealed by radon-rejecting tape. In order to evaluate the initial activity concentrations of those radionuclides in the materials, the grain size fraction <2 mm was measured for 24 h in a 60 mL cylindrical box. This measuring geometry also enables ^{234}Th and ^{210}Pb corrections for self-absorption as proposed in Ref. [4]. For the gamma-spectrometric measurement of the extraction liquids, a special geometry based on 250 mL Marinelli beakers was introduced by using waste water, which bears several artificial radionuclides covering the energy range 60–1330 keV. It was provided by the German Federal Office for Radiation Protection (BfS) and has been validated by more than 280 intercomparison measurements. A control measurement of the prepared calibration standard was undertaken with a second gamma-spectrometry system standing in the Laboratorium Radiometrii of the Polish Central Mining Institute (GIG), Katowice.

The detection limit of the gamma-spectrometry calibrated in this way is 0.5 Bq/L for ^{226}Ra and slightly higher for other radionuclides. However, before the gamma spectrometric measurements were started, all the extraction reagents as well as the calibration standard were solidified in order to avoid precipitation of particles on the Marinelli beaker bottom. After exact determination of the liquid volume, the solidification was done by adding Agar-Agar into the liquid heated to about 80°C. The Marinelli beaker was then put into boiling water for at least 10 min. Subsequently, it was allowed to cool down slowly.

TABLE 2. RELEVANT RADIONUCLIDES OF THE ^{238}U AND ^{232}Th DECAY SERIES

Radionuclide	Measured via	Gamma line(s)
^{238}U	^{234}Th after storage for 80 days	63.3 keV
^{226}Ra	^{214}Pb ^{214}Bi after storage for 3 weeks	295 keV and 351 keV 609 keV and 1120 keV
^{210}Pb	Directly	46.3 keV
^{228}Ra	^{228}Ac after storage for 36 h	911 keV and 969 keV
^{228}Th	^{208}Tl to be multiplied by 3 after storage for 3 weeks	583 keV and 860 keV

In order to determine the radionuclides activity concentrations dissolved in each extractant as a proportion of the starting solid material, it was necessary to calculate the volume activity concentration of the extraction liquids in relation to the activity concentration in the dry mass. That was possible because the amount of starting material was weighted carefully before the extraction was undertaken. Therefore, the activity concentration of each extraction liquid represented a percentage of the dry mass activity concentration of the starting material. The relationship between the activity concentration of the liquid (i.e. $\text{activity}_{\text{liquid}}$) and that of the dry mass (i.e. $\text{activity}_{\text{solid}}$) is given by equation (1):

$$\text{activity}_{\text{solid}}[\text{Bq/kg}] = \frac{1000}{\frac{1000}{\text{vol}_{\text{liquid}}[\text{mL}]} \cdot \text{weight}_{\text{materialextracted}}[\text{g}]} \cdot \text{activity}_{\text{liquid}}[\text{Bq/L}] \qquad (1)$$

factor for correlation of extraction liquid given in [mL] up to 1 L

factor for correlation of volume extraction liquid up to weighted amount of material given in [g] filled in centrifugal cups and relation to 1 kg

The residuals from the extraction procedures were discarded due to the fact that their volumes, especially of the BCR scheme, were much too small for reliable gamma spectrometric measurements. Therefore, the radionuclide concentrations remaining in those residuals were calculated by subtracting the total sum of the activities stored in the extraction reagents from the initial radionuclide content.

3. Manufacturing processes and initial radionuclide concentrations

3.1. Aluminium production

The raw material for aluminium production is bauxite and that for the Romanian processing plant located close to the eastern city Tulcea comes from the Brazilian Trombeta zone and the Boke deposit in Guinea Bissau [5]. The aluminium oxides in the bauxite are extracted according to the so-called Bayer process, which generates huge amounts of red sludge as the remaining waste from thickening of the aluminium hydroxides. The Boke bauxite contains ^{226}Ra at 230 Bq/kg and ^{210}Pb at 420 Bq/kg; the bauxite from the Trombeta zone contains ^{226}Ra at 2000 Bq/kg and ^{210}Pb at 4000 Bq/kg. The Tulcea red sludge was found to contain ^{226}Ra at 190 Bq/kg and ^{210}Pb at 330 Bq/kg.

3.2. Refractory industry

One important refractory product is mullite, for which manufacturing process starts with a mixture of either alumina and silica or bauxite and kaolin to be loaded into an electric arc furnace with temperatures exceeding 2000°C [6]. There, the materials are calcined and transformed into the liquid state by fusion processes. The initial chemical combination Al_2SiO_5 is no longer available to be converted into unbound Al_2O_3 and free silica, and the result is mullite ($3Al_2O_3{\cdot}2SiO_2$). In order to further increase the mullite hardness, zircon sand providing the heavy mineral zirconium is also added into the arc furnace. The resulting product is then called fused zirconia–mullite (FZM). During the melting in the furnace, a large amount of dust is generated, which is collected by air filters. The raw material zircon sand contains 2750 Bq/kg ^{226}Ra, the FZM product 1600 Bq/kg ^{226}Ra and 1000 Bq/kg ^{210}Pb, whereas the filter dust sample is exclusively contaminated by 162 000 Bq/kg ^{210}Pb.

3.3. Fertilizer production

As the raw material for the Belgian fertilizer production, one of the types of phosphate ore used is imported from Morocco, which is of sedimentary origin and contains ^{238}U at 1200 Bq/kg, ^{226}Ra at 1500 Bq/kg and ^{210}Pb at 1600 Bq/kg. In terms of the wet production process for multi-nutrient (MN) fertilizers, the phosphate rock is mixed with sulphuric acid (H_2SO_4) for converting the insoluble phosphate portion into soluble phosphoric acid (H_3PO_4), which also produces 5 t of phosphogypsum waste per tonne of phosphoric acid [7]. The by-product is single superphosphate (SSP), which is a starting material for the MN fertilizers or further processed for triple superphosphate (TSP), also needed for that fertilizer type. The investigated fertilizer of PK type (representative of MN fertilizers) generally contains more than 750 Bq/kg ^{238}U and about 160 Bq/kg of ^{226}Ra and ^{210}Pb, whereas the phosphogypsum sample is proven for all the relevant radionuclides of both decay series not to exceed 200 Bq/kg.

3.4. Hard coal mining

In terms of underground hard coal mining activities, it is usually necessary to pump groundwater to the surface. Depending on the geological background, those waters can be strongly enriched in radium isotopes [8]. Once on the surface, the presence of barium in river water into which pit water is discharged can result in radium precipitation along the river under oxidizing conditions forming a solid called radiobarite [$Ba(Ra)SO_4$]. This phenomenon is also known from discharged radium bearing waste waters of phosphate fertilizer production [9]. The sediments collected from a sewer in the Northern Ruhr-district contain only ^{226}Ra (sediment 1: 540 Bq/kg; sediment 2: 1300 Bq/kg; sediment 3: 1250 Bq/kg) and ^{210}Pb growing again (sediment 1: 330 Bq/kg; sediment 2: 650 Bq/kg; sediment 3: 520 Bq/kg); ^{228}Ra is never detected.

3.5. Thorium contaminated soils

In Germany, two special sites are known to be contaminated especially by ^{232}Th progeny [10]. At one location, residues of thorium–cobalt catalysts, which had formerly been used in connection with the so-called FISCHER-TROPSCH synthesis for producing synthetic fuels by hydrogenation of coal, were disposed of. The second site became contaminated by thorium-bearing dust when a thorium processing gas mantle plant had been destroyed by an air raid at the end of the Second World War and the dust was widely spread in the vicinity of the factory. Soil 1 contaminated by the residue was found to contain ^{238}U 10 000 at Bq/kg, ^{226}Ra at 1000 Bq/kg, ^{228}Ra at 501 000 Bq/kg and ^{228}Th at 420 000 Bq/kg. Both the other soils are derived from the former gas mantle factory — soil 2 contains ^{238}U at 2200 Bq/kg, ^{226}Ra at 1200 Bq/kg, ^{210}Pb at 2000 Bq/kg, ^{228}Ra at 11 000 Bq/kg and ^{228}Th at 9300 Bq/kg, and soil 3 contains ^{238}U at 1600 Bq/kg, ^{226}Ra at 880 Bq/kg, ^{210}Pb at 1600 Bq/kg, ^{228}Ra at 8900 Bq/kg and ^{228}Th at 7600 Bq/kg.

3.6. Crude oil exploitation

The exploitation of crude oil and natural gas are very often connected with strong enhancements especially of radium isotopes, ^{210}Pb and ^{228}Th [11]. Two different types of TENORM are typically generated during those exploitation processes: if barium is dissolved in the produced brines, it precipitates inside the pipeline walls and other installations as scale due to pressure and temperature changes and radium-isotopes are then co-precipitated as radiobarite ($Ba(Ra)SO_4$), the much higher ^{210}Pb concentrations are caused by exhaled radon from oily materials in volatile dense areas (e.g. pipelines, vessels or storage tanks). Contaminated sludge results from the drilling process itself or is left behind in the sumps of separation vessels. The scale sample analysed was found to contain ^{226}Ra at 9200 Bq/kg, ^{210}Pb at 45 600 Bq/kg, ^{228}Ra at 1400 Bq/kg and ^{228}Th at 1800 Bq/kg. The sludge contains 48 100 Bq/kg of ^{226}Ra, 46 100 Bq/kg of ^{210}Pb, 12 800 Bq/kg of ^{228}Ra and 13 000 Bq/kg of ^{228}Th.

4. Results and conclusions

All the radionuclide portions dissolved per extraction fraction are presented in Fig. 1.

(a) Aluminium production:
Both the raw materials contain enhanced radionuclide concentrations and show comparable leaching behaviour, especially the Trombeta bauxite provides ^{226}Ra and ^{210}Pb for the easily exchangeable fraction by 55% respectively 20% being roughly equivalent to 900 Bq/kg each. In addition, ^{226}Ra is also determined to be available for plants by 40% corresponding to 800 Bq/kg. 40% of ^{226}Ra, which means 80 Bq/kg, are both water soluble and also easily exchangeable from the Tulcea red sludge. Due to the relatively low radionuclide concentrations in that waste, the transfer seems to be diluted during the aluminium production process.

(b) Refractory industry:
From the additive zircon sand only small amounts of ^{226}Ra are dissolved within the whole BCR procedure (10%) due to the radionuclides' strong fixation in the zircon crystal lattice. Concerning the product FZM, 20% of the initial ^{226}Ra is bond to the oxidizable fraction, lead is left in the residue. Since the fusion process raises temperatures where ^{210}Pb (besides ^{222}Rn and ^{210}Po) is removed from the production process, the generated filter dust is highly contaminated by ^{210}Pb concentrations of more than 160 000 Bq/kg, from which 10% are bond to iron and manganese oxides and 30% are fixed on sulphides.

(c) Fertilizer production:
The Moroccan phosphate ore is characterized by ^{226}Ra mostly (50%) bond to organic matter and sulphides, which are the main rock components due to the phosphorite forming by animal particles. The strongest enhanced uranium of the produced PK fertilizer is plant available by 45% and water soluble (30%) as well, which is to be expected for a fertilizer. Its uranium concentration is caused by the phosphoric acid associated with the wet process, because it leaches almost all the uranium from the initial rock and transfers it into the product. By definition, the waste material phosphogypsum is not TENORM, but provides almost all the initial lead content (45 Bq/kg) for plants. Its generally low activity concentrations can be explained by the unbalanced ratio (5 : 1) of huge phosphogypsum amounts compared with the produced phosphoric acid volume.

(d) Hard coal mining:
The contaminated sediments are determined not to provide one of the enriched ^{226}Ra and lead radionuclides under any of the investigated chemical conditions. This can be explained by the very stable crystalline structure of the radiobarite they are fixed in, so that solutions used are not sufficiently aggressive to disrupt and remove compounds. This result is in good accordance with Ref. [12]. The very well corresponding amounts of ^{228}Th present in all the three BCR fractions of all sediments can be neglected due to very low initial activity concentrations (< 200 Bq/kg).

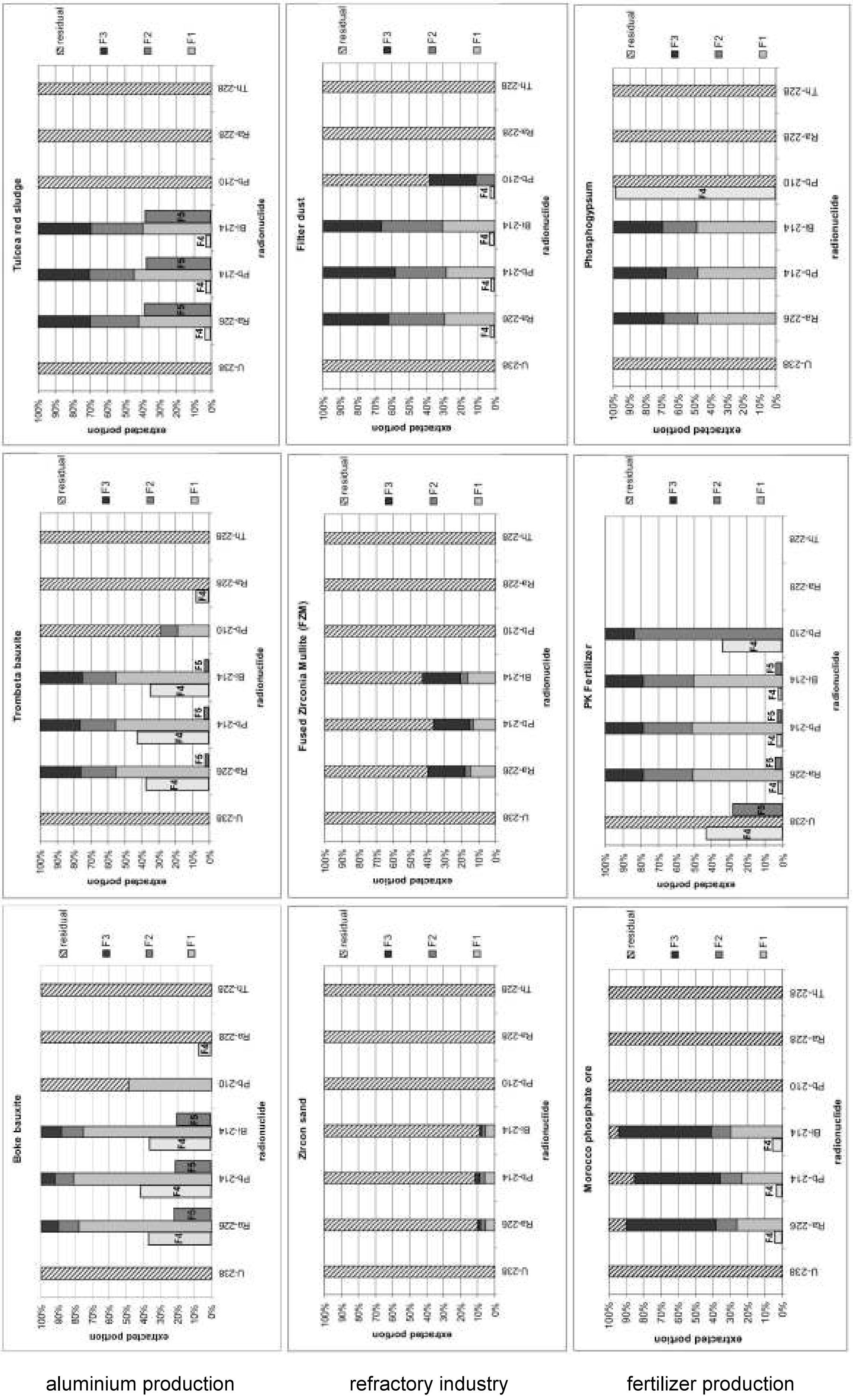

FIG. 1. Dissolved radionuclide fractions from raw materials, products and wastes

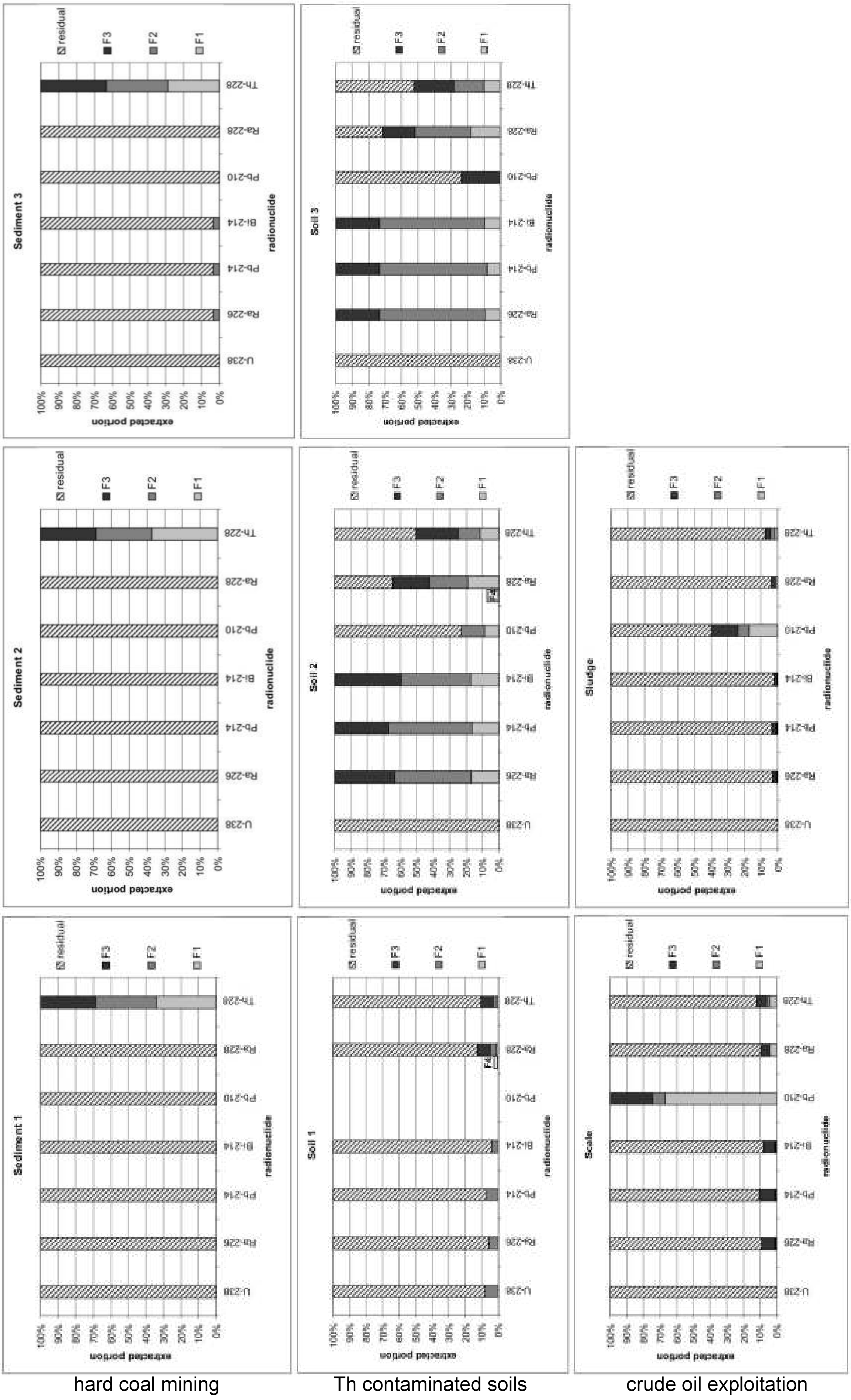

FIG. 1. Dissolved radionuclide fractions from raw materials, products and wastes

(e) Thorium contaminated soils:
By far the highest activity concentrations are found in the thorium contaminated soils. The low leaching coefficients for ^{228}Ra and ^{228}Th of soil 1 are put into perspective by their extremely high initial concentrations, so 2% each are fixed in the reducible fraction (10 000 Bq/kg) and 8% in the oxidizable one (40 000 Bq/kg), 2% of ^{228}Ra are also plant available. In soil 2, roughly 20% of ^{228}Ra (2200 Bq/kg) can be found in each of the BCR fractions and 8% (900 Bq/kg) are plant available, 12% of ^{228}Th are easily exchangeable and reducible respectively, 25% are bound to organic matter and sulphides. Soil 3, taken at the same site, shows similar types of radionuclides bonding, just the initial activity concentrations, which are also of same ratios, are slightly lower.

(f) Crude oil exploitation:
All the ^{210}Pb concentration contained in the scale is completely leached in terms of the BCR procedure, 65% (almost 30 000 Bq/kg) are easily exchangeable, 10% (4700 Bq/kg) are bound to iron and manganese oxides and 25% (12 000 Bq/kg) are fixed on organic matter and sulphides. The sludge sample is determined for a similar initial ^{210}Pb and also ^{226}Ra concentration, but most of them are left in the residue. 18% of lead are easily exchangeable (8300 Bq/kg), 6% (2800 Bq/kg) are fixed in the reducible fraction and 18% in the oxidizable one. The mentioned ^{226}Ra is only detected in the last BCR fraction by 3%, which means 1400 Bq/kg.

(g) Procedure:
As the analyses show, the measuring procedure developed is reliable and leads to comparable and reproducible results, i.e. samples from same sources are determined for the same types of radionuclide bonding. This is proven by all the extraction liquids of the three sediments from hard coal mining influenced environment and the leaching coefficients of the highly thorium contaminated soils 2 and 3 as well.

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