



Partitioning of radionuclides and trace elements in phosphogypsum and its source materials based on sequential extraction methods

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Abstract

Phosphogypsum is a waste produced by the phosphate fertilizer industry. Although phosphogypsum is mainly calcium sulphate dihydrate, it contains elevated levels of impurities, which originate from the source phosphate rock used in the phosphoric acid production. Among these impurities, radionuclides from ²³⁸U and ²³²Th decay series are of most concern due to their radiotoxicity. Other elements, such as rare earth elements (REE) and Ba are also enriched in the phosphogypsum. The bioavailability of radionuclides (²²⁶Ra, ²¹⁰Pb and ²³²Th), rare earth elements and Ba to the surrounding aquatic system was evaluated by the application of sequential leaching of the phosphogypsum samples from the Brazilian phosphoric acid producers. The sequential extraction results show that most of the radium and lead are located in the “iron oxide” (non-CaSO₄) fraction, and that only 13–18% of these radionuclides are distributed in the most labile fraction. Th, REE and Ba were found predominantly in the residual phase, which corresponds to a small fraction of the phosphate rock or monazite that did not react and to insoluble compounds such as sulphates, phosphates and silicates. It can be concluded that although all these elements are enriched in the phosphogypsum samples they are not associated with CaSO₄ itself and therefore do not represent a threat to the surrounding aquatic environment.

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1. Introduction

The presence of natural radionuclides in mineral ores and their redistribution in products and wastes has been well known. Among industrial wastes containing technologically enhanced naturally occurring radioactive materials (TENORM), excluding those generated by nuclear technology, of particular concern is phosphogypsum. This waste is produced by precipitation during wet sulphuric acid processing of phosphate rocks, thus posing serious problems with its utilisation and safe disposal. In Brazil, the main phosphate industries are responsible for the production of approximately 23.5×10^6 metric tonnes of phosphogypsum waste per year. Most of this phosphogypsum waste is disposed as above ground piles in Cubatão at a rate of 4×10^6 kg per day.

Phosphogypsum produced during the process is filtered off and pumped as slurry to nearby ponds, where it stays for a period sufficient to allow complete deposition. This waste is then moved to nearby storage areas. Santos et al. (2001) performed the characterization of natural radionuclides of the U and Th series in the stockpiled phosphogypsum waste in Cubatão, where are located two main producers, named A and C. As a complementary study, trace and microelements (Ba, Co, Cr, Fe, Hf, Sb, Sc, Ta, Th, U, and rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) were also determined in the samples (Santos et al., *in press*). The aquatic environment near the disposal area was assessed by measuring natural radionuclide's activity in monitor wells, river water and sediment samples. Activities up to 2.9 and 3.1 Bq L⁻¹ were observed for Ra-226 and Pb-210 in the monitor wells in the vicinity of the piles; whereas Ra-228 reached concentrations up to 8.0 Bq L⁻¹. Sediments from rivers, in the area of influence of the stacks, presented higher concentrations of U, Th, all rare earth elements (except Tb, Yb and Lu), Hf, As and Zr (Santos et al., *in press*).

Since one of the prime concerns about phosphogypsum storage is the potential for contamination of fresh water aquifers underlying the stacks, one important environmental question is to define the actual site of radionuclides within the solid phosphogypsum materials. The radionuclides can be uniformly distributed throughout the lattice structure of phosphogypsum or can be contained in separate, distinct mineral phases. The important issue is to know not only how much is there but also how it is included in the sample and therefore how much is available to the surrounding environment. The main purpose of this study is to evaluate the availability of radionuclides (²²⁶Ra, ²¹⁰Pb and ²³²Th), rare earth elements and Ba to the aquatic system under the influence of the stacks. Similar study was undertaken by Burnett et al. (1999), with phosphogypsum from Florida. Their conclusion, however, cannot be applied directly, since the phosphate rock and the chemical process vary for different industries. One approach that gives useful information is the application of sequential leaching of soils defined by Tessier et al. (1979), which was designed originally to evaluate the distribution of transition metals within five extraction phases. Since phosphogypsum is in a water-soluble phase, a deionized water extraction was added as an initial step in addition to the five extractions defined by Tessier (Burnett et al., 1999). The reagents used for the six extractions are designed to indicate the relative amounts of radionuclides in the following fractions: (1) deionized water → water-soluble; (2) MgCl₂ → ion exchangeable; (3) NaOAc/HOAc → carbonate; (4) NH₂OH·HCl/HOAc → iron oxide; (5) HNO₃/H₂O₂ → organic matter; and (6) total dissolution by hot acid attack → silicate residue.

2. Materials and methods

Activity concentrations of ²²⁶Ra, ²²⁸Ra and ²¹⁰Pb were measured, in 21 samples of phosphate rock and phosphogypsum, by gamma spectrometry with a hyper-pure germanium detector, GEM-15200, from

EG&G Ortec, with a resolution of 1.8 keV for the 1332 keV ^{60}Co photopeak, for 4096 channels. The detector was calibrated using natural soil, rock and water spiked with radionuclides certified by Amersham. Samples were packed in 100 cm³ cans and sealed for about four weeks prior to the measurement in order to ensure that equilibrium has been reached between ^{226}Ra and its decay products of short half-life. The ^{226}Ra activities were determined by taking the mean activity of the three separate photopeaks of its daughter nuclides: ^{214}Pb at 295 keV and 352 keV, and ^{214}Bi at 609 keV. The ^{228}Ra content of the samples was determined by measuring the intensities of the 911 keV and 968 keV gamma-ray peaks from ^{228}Ac . The concentration of ^{210}Pb was determined by measuring the activity of its low energy peak (47 keV). Self-absorption correction was applied since the attenuation for low energy gamma rays is highly dependent upon sample composition. The approach used was that suggested by Cutshall et al. (1983). Typical lower limits of detection for gamma spectrometry were 4.5 Bq kg⁻¹ for ^{226}Ra , 3.1 Bq kg⁻¹ for ^{228}Ra and 25 Bq kg⁻¹ for ^{210}Pb , for a counting time of 50,000 s.

The sequential extraction analysis was carried out in triplicate using phosphogypsum samples from the two main Brazilian producers of phosphoric acid: named A and C. Activity concentrations of ^{226}Ra and ^{210}Pb were measured in samples of phosphogypsum by gamma spectrometry with a hyper-pure germanium detector, GEM-15200, from EG&G Ortec. The procedure is the same as described for the characterization of phosphate rock and phosphogypsum.

Trace and microelements (Ba, Fe, Hf and Sc), rare earths (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), U and Th were determined by instrumental neutron activation analysis (INAA). The elements determination was carried out by irradiation of approximately 150 mg of each sample, during 16 h at a neutron flux of 10^{12} n cm⁻² s⁻¹, at Instituto de Pesquisas Energéticas e Nucleares (IPEN) research reactor IEA-R1. The induced radioactivity was measured with a Ge-hyper-pure detector, Inter technique, with 2.1 keV resolution for the 1332 keV Co-60 photopeak. The concentration of the analysed elements was determined by comparing activities obtained in the samples with standard materials Buffalo River Sediment (NIST-2704) and Soil-7 (IAEA).

Sequential leaching was carried out by using an accurately weighed, approximately 2.8 g of each phosphogypsum samples, dried and ground. The solutions used in the sequence consisted of 2 L of deionized water with agitation; 16 mL of 1 M MgCl₂ with agitation for 1 h, the sample was washed two times with deionized water and centrifuged; 16 mL of 1 M NaOAc/HOAc at pH 5.0 with agitation for 1 h, the sample was washed and centrifuged; 40 mL of 0.04 M NH₂OH·HCl in 25% acetic acid, the sample was heated at 96 ± 3 °C for 6 h, washed and centrifuged; 6 mL of 0.02 M HNO₃ and 10 mL of 30% H₂O₂, the sample was heated at 85 ± 2 °C for 2 h and the procedure was repeated with the addition of 6 mL H₂O₂ and the solution washed and centrifuged; total dissolution of the final residue by heating with HNO₃, HCl and HF, sequentially, until total dissolution. All supernatant solutions for each sequential step were combined for the analysis of ^{226}Ra and ^{210}Pb by radiochemical separation and measurement of total alpha and beta counting on a gas flow proportional counter. This procedure consisted of an initial precipitation of Ra and Pb with 3 M H₂SO₄, dissolution of the precipitate with nitro-tri-acetic acid at basic pH, precipitation of Ba(^{226}Ra)SO₄ with ammonium sulphate and precipitation of $^{210}\text{PbCrO}_4$ with 30% sodium chromate. The ^{226}Ra concentration was determined by gross alpha counting of Ba(^{226}Ra)SO₄ precipitate and ^{210}Pb concentration through its decay product ^{210}Bi , by measuring the gross beta activity of $^{210}\text{PbCrO}_4$ precipitate. The chemical yields for both radionuclides were determined gravimetrically by weighing both precipitates. Typical lower limits of detection were 2.2 mBq L⁻¹ for ^{226}Ra and 4.9 mBq L⁻¹ for ^{210}Pb .

All residual phases of each sequential step were used for the elemental characterization by measuring the residues by INAA.

3. Results and discussion

The elemental and radioactive characterizations of phosphogypsum and the phosphate rock used as raw material in industries A and C are presented in Tables 1–3. Although the origin of

Table 1
Activity concentration in rock and phosphogypsum samples from industries A and C (Bq kg⁻¹)

	Industry A		Industry C	
	Mean	Range	Mean	Range
<i>Phosphate rock (n = 9)</i>				
²³⁸ U	1151	102–1642	650	347–1163
²³² Th	294	258–435	390	246–407
²²⁸ Ra	283	209–1171	287	207–565
²²⁶ Ra	328	239–862	348	255–427
²¹⁰ Pb	843	329–1414	495	379–666
<i>Phosphogypsum (n = 12)</i>				
²³⁸ U	40	32–69	48	37–61
²³² Th	273	208–346	175	61–285
²²⁸ Ra	247	198–280	214	90–238
²²⁶ Ra	811	558–1251	350	307–594
²¹⁰ Pb	813	539–1234	353	303–581

n = Number of samples analysed.

the two rocks is the same, both are extracted from do Catalão I carbonatite complex, located in central Brazil, their composition is slightly different as far as the natural radionuclides are concerned. The ratio of U/Th in the rock samples of both industries (4 and 1.6) is quite different. Rock sample from industry A presents value similar to that of the crust rock (Turekian and Wedepohl, 1961), rock C, on the other hand, is enriched in U by a factor of 2.5. The results of Table 1 for the ratios U/²²⁶Ra and Th/²²⁸Ra confirm that the various members of the U and Th decay series are in approximate equilibrium in the two rock samples.

Oliveira and Imbernon (1998) investigated the geochemistry and mineralogy of the Catalão I carbonatite complex weathering profile from where the source phosphate rock for the two

Table 2
Rare earth elements concentration in rock and phosphogypsum samples from industries A and C (µg g⁻¹)

	Industry A		Industry C	
	Mean	Range	Mean	Range
<i>Phosphate rock</i>				
La	1655	1086–2002	2124	1303–2510
Sm	254	140–18,512	268	154–26,003
Nd	1555	851–1967	2202	2026–5570
Ce	4114	2808–5267	4346	3443–5409
Tb	10	5–11	12	5–20
Eu	62	40–67	67	45–73
Lu	0.5	0.4–0.6	0.6	0.4–0.8
Yb	10	6–13	10	9–17
<i>Phosphogypsum</i>				
La	1239	807–1625	1300	155–2373
Sm	156	113–208	149	23–274
Nd	1291	1087–1511	1285	147–1722
Ce	2490	1998–2877	2574	307–3387
Tb	7	5.4–9.2	7.3	2–10
Eu	41	34–65	36	5.2–47
Lu	0.21	0.15–0.29	0.4	0.1–0.5
Yb	4	2.5–6.5	4.3	2.6–9.8

Table 3

Elemental concentration in rock and phosphogypsum samples from industries A and C ($\mu\text{g g}^{-1}$)

	Industry A		Industry C	
	Mean	Range	Mean	Range
<i>Phosphate rock</i>				
Hf	13	2–14	10	6–21
Sc	21	17–22	22	15–29
Fe	11,722	2156–18,707	12,061	11,123–22,597
Ba	1633	1207–6963	12,884	5583–19,974
<i>Phosphogypsum</i>				
Hf	2	1.3–8.3	3	1–4
Sc	4	1.2–4	4.5	0.6–8.4
Fe	1358	128–2372	3996	565–21,387
Ba	6019	1810–10,433	2839	964–5010

industries is extracted. The fresh rock is a phoscorite (igneous rock made up of apatite, magnetite and olivine) cut by abundant carbonatitic veins (carbonatite is an igneous rock with more than 50% of carbonates). Both parent rocks show LREE enrichment, but LREE/HREE ratio is higher for carbonatite. The weathered products contain apatite, which occurs together with goethite and quartz, and small amounts of secondary Al-phosphates, magnetite, anatase and barite. Chemically, they are characterized by low contents of MgO and SiO₂ and high P₂O₅ and CaO contents. Correlation analysis was applied to the results of the phosphate rock concentration available for the two industries, A and C (Table 4). In both cases, Th correlates well with REE and especially well with the light rare earth elements (LREE). These elements are probably enriched in the Al-phosphate mineral together with monazite ((Ce, La, Y, Th)PO₄). Uranium, on the other hand, is present in the apatite mineral. Good correlations were also found for the members of U-series (²²⁶Ra and ²¹⁰Pb). The rock samples used as raw material in the industries are treated for the removal of iron compounds before entering into the process. This fact could explain the lack of correlation for the Th series.

Table 4

Correlation analysis applied to the results of the phosphate rock of the two industries

	La	Sm	Nd	Ce	Tb	Eu	Lu	Yb	U	Hf	Sc	Th	Fe	Ba	²²⁸ Ra	²²⁶ Ra	²¹⁰ Pb
La	1.00																
Sm	0.94	1.00															
Nd	0.23	-0.07	1.00														
Ce	0.89	0.87	0.15	1.00													
Tb	0.88	0.83	0.24	0.90	1.00												
Eu	0.95	0.98	0.21	0.92	0.89	1.00											
Lu	0.40	0.53	0.57	0.46	0.65	0.54	1.00										
Yb	0.61	0.44	-0.09	0.76	0.69	0.53	0.16	1.00									
U	-0.02	0.38	-0.34	-0.34	0.12	0.01	-0.03	-0.48	1.00								
Hf	0.24	0.20	-0.06	0.41	0.62	0.28	0.45	0.65	-0.21	1.00							
Sc	0.45	0.58	0.32	0.20	0.27	0.50	0.14	-0.22	0.37	-0.26	1.00						
Th	0.88	0.88	0.24	0.86	0.86	0.87	0.31	0.53	-0.17	0.18	0.48	1.00					
Fe	0.29	0.31	-0.07	0.38	0.58	0.29	0.24	0.56	-0.13	0.91	-0.07	0.32	1.00				
Ba	0.49	0.42	0.76	0.29	0.50	0.42	0.35	0.06	-0.08	0.14	0.64	0.47	0.32	1.00			
²²⁸ Ra	0.12	0.31	-0.49	0.38	0.32	0.15	-0.02	0.52	-0.23	0.53	-0.53	0.30	0.54	-0.42	1.00		
²²⁶ Ra	-0.33	-0.11	-0.46	-0.40	-0.10	-0.22	0.08	-0.26	0.68	0.09	-0.03	-0.53	-0.10	-0.44	-0.18	1.00	
²¹⁰ Pb	-0.69	-0.66	-0.43	-0.67	-0.59	-0.67	-0.27	-0.24	0.27	-0.07	-0.39	-0.78	-0.28	-0.63	-0.16	0.77	1.00

By comparing the concentration of the elements in the phosphate rock and in phosphogypsum (Tables 1–3), it is clear that this equilibrium is significantly disrupted during the chemical processing of the phosphate rock. In a previous paper Mazzilli et al. (2000) showed that during the treatment of phosphate rock with sulphuric acid U is enriched in the phosphoric acid whereas thorium and radium isotopes and Pb-210 are enriched in the phosphogypsum. The fractioning of REE and the other elements analysed is shown in Fig. 1, where the ratio of the elemental mean concentration in phosphogypsum over the elemental mean concentration in the phosphate rock (both concentrations normalized by Sc mean concentration) is presented. The wide variation observed in Ba concentration can be explained by the variation in the pre-treatment of the phosphate rock in both industries. Another fact that can also contribute is the recrystallization process that raises the BaSO₄ concentration over the CaSO₄ concentration due to the major solubility of the latter (Degetto et al., 1999).

It can be seen that REE, Ba, ²²⁶Ra, ²¹⁰Pb, ²³²Th and ²²⁸Ra are enriched in phosphogypsum. In the phosphogypsum samples (Table 5), ²³²Th, ²²⁸Ra, REE and Ba correlate well, indicating that these elements are probably in a residual phase as insoluble phosphates (Th and REE), sulphates (Ba) or unreacted monazite. The radionuclides ²²⁶Ra and ²¹⁰Pb also present high correlation, indicating that these elements behave in the same way during the chemical attack of the rock sample.

Results obtained for ²²⁶Ra and ²¹⁰Pb in the sequential extraction experiments are presented in Fig. 2. The results concerning the behaviour of chemical elements and rare earth element in the sequential extraction experiments are also presented in Fig. 2. Results from the sequential extraction show that there are no significant variations in the extraction profiles for ²²⁶Ra and ²¹⁰Pb in the various fractions among different types of phosphogypsum samples. Most of these radionuclides are found in the iron oxide fraction (41–55%), whereas amounts ranging from 13 to 18% were uniformly distributed in the first (most labile fraction) and the following two

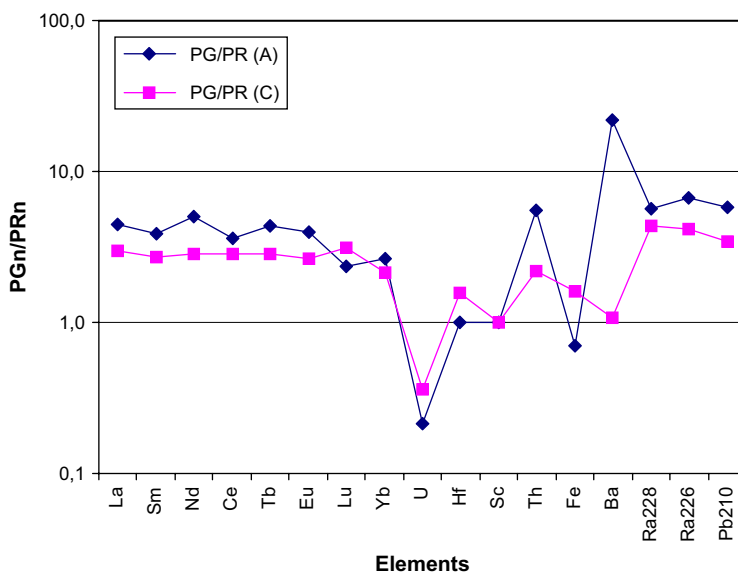


Fig. 1. Enrichment factor: elemental concentration in phosphogypsum/elemental concentration in phosphate rock, both normalized by Sc (PGn/PRn).

Table 5

Correlation analysis applied to the results of the phosphogypsum of the two industries

	La	Sm	Nd	Ce	Tb	Eu	Lu	Yb	U	Hf	Sc	Th	Fe	Ba	²²⁸ Ra	²²⁶ Ra	²¹⁰ Pb
La	1.00																
Sm	0.98	1.00															
Nd	0.88	0.81	1.00														
Ce	0.95	0.89	0.98	1.00													
Tb	0.87	0.78	0.99	0.97	1.00												
Eu	0.95	0.89	0.98	1.00	0.98	1.00											
Lu	-0.45	-0.49	-0.69	-0.61	-0.64	-0.62	1.00										
Yb	0.88	0.91	0.54	0.69	0.54	0.68	-0.12	1.00									
U	-0.69	-0.72	-0.49	-0.57	-0.55	-0.61	0.23	-0.76	1.00								
Hf	-0.72	-0.64	-0.45	-0.57	-0.49	-0.56	-0.29	-0.80	0.54	1.00							
Sc	-0.02	0.00	-0.16	-0.09	-0.26	-0.16	0.22	0.06	0.60	-0.09	1.00						
Th	0.96	0.89	0.94	0.98	0.93	0.97	-0.44	0.75	-0.54	-0.72	0.02	1.00					
Fe	-0.41	-0.50	-0.28	-0.32	-0.33	-0.37	0.38	-0.49	0.89	0.11	0.73	-0.22	1.00				
Ba	0.97	0.99	0.76	0.86	0.75	0.86	-0.38	0.95	-0.77	-0.71	-0.03	0.88	-0.52	1.00			
²²⁸ Ra	0.82	0.77	0.93	0.92	0.88	0.90	-0.73	0.49	-0.24	-0.33	0.17	0.88	-0.06	0.70	1.00		
²²⁶ Ra	-0.52	-0.42	-0.51	-0.54	-0.45	-0.49	0.04	-0.35	-0.21	0.54	-0.69	-0.66	-0.56	-0.40	-0.67	1.00	
²¹⁰ Pb	-0.58	-0.49	-0.55	-0.59	-0.49	-0.54	0.08	-0.42	-0.15	0.58	-0.67	-0.70	-0.50	-0.47	-0.71	1.00	1.00

extractions phases (ion exchangeable and carbonate fractions, respectively). It is also interesting to note that the behaviour of Ra and Pb is the same for the phosphogypsum of the two industries studied, providing further evidence that the primary rock used as raw material is the same for the two industries. This behaviour is overstated by the high correlation observed for these two elements in the phosphogypsum. It can be concluded that the availability of Ra and Pb is not predominant in the soluble fraction that corresponds to the environmental conditions such as water percolation as rain. It should be noted that in the first step added to the sequential extraction, a soluble phase with deionized water, the PG/H₂O mass ratio was sufficient to reach the solubility of phosphogypsum in water. In this phase the weight loss of phosphogypsum was about 85%, showing that most of the Ra and Pb present in the phosphogypsum are not associated with the soluble calcium sulphate phase.

The sequential extraction results show that most of the radium and lead are located in water-insoluble (non-CaSO₄) fractions. Burnett and Hull (1996) investigated the geochemistry of some water-insoluble residues from gypsum samples, by ICP analysis. The results showed that ²²⁶Ra correlates well with trace metals Ba, Sr, La, Ce and Pb and the major elements Al, P and Fe. They suggested that barium sulphate could be an important carrier phase for radium, since BaSO₄ is known to be extremely insoluble and barium is always present as a minor element in phosphorites. However, they also found that the amount of sulphate remaining on a molar basis was too little to support the amount of barium and strontium contained in the same material as a separate phase. Another possibility to explain the presence of radionuclides in a water-insoluble phase was suggested by Kramer and Curwick (1990), who found that ²²⁶Ra was present in a minor insoluble phase identified as aluminium phosphate. This mineral is known to contain appreciable amount of strontium, barium, iron and rare earth elements.

The results obtained in the sequential extraction experiments show that Th, Ba and REE were found predominantly in the residual phase. The X-ray diffraction technique was applied to the phosphogypsum itself and to the residues obtained in the sequential extraction. It was observed that phosphogypsum samples are predominantly dihydrate calcium sulphate and

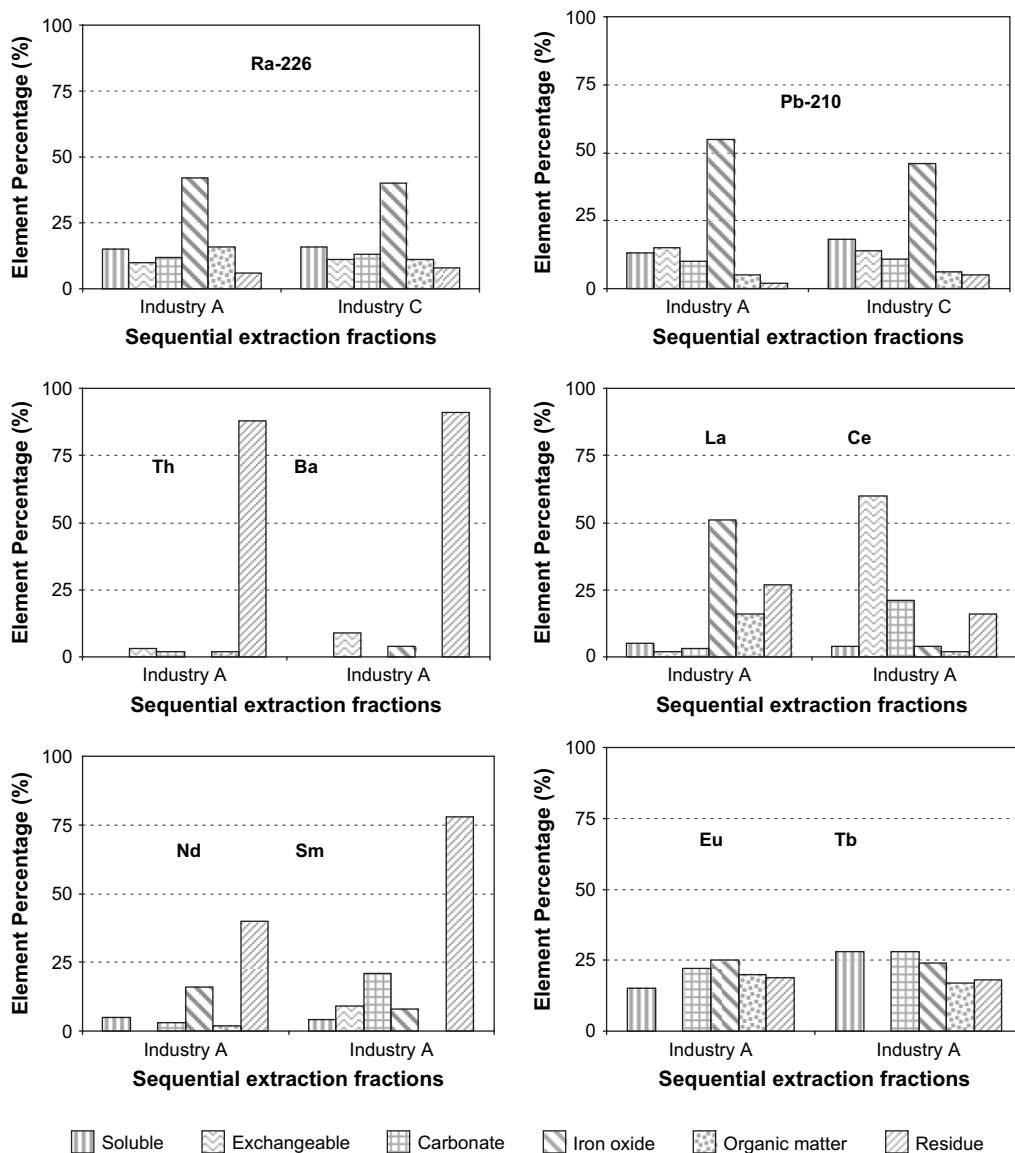


Fig. 2. Results obtained from the sequential extraction experiment.

that silica (SiO_2) and barium sulphate are present in all the residual phases of the sequential extraction. Therefore, the final residual phase corresponds to a small fraction of the phosphate rock or monazite and to insoluble compounds such as sulphates, phosphates and silicates, which were formed during the chemical attack with sulphuric acid.

The rare earth elements are usually found in more resistant minerals, such monazite, which explains their presence in the less soluble fractions. One exception was cerium, which was found mainly in the exchangeable fraction, probably due to its oxidation states (Ce^{3+} and Ce^{4+}), Ce^{3+} being more soluble than Ce^{4+} . According to Toledo et al. (2004), the Ce present in the carbonatite

from Catalão, has an oxidation state of +4. During the chemical attack for the production of phosphoric acid, Ce is probably reduced to the oxidation state +3 more soluble and is more easily leached. Eu and Tb presented a uniform distribution in the fractions of the sequential extraction, except for the exchangeable fraction, in which their concentrations were below the detection limits. This behaviour is probably due to the fact that these elements are present in distinct phases like accessory minerals or in different mineral phases due to isomorphic substitution.

4. Conclusion

It can be concluded that ^{226}Ra , ^{210}Pb , ^{232}Th , ^{228}Ra , REE and Ba are enriched in the phosphogypsum during the treatment of phosphate rock with sulphuric acid. Sequential extraction experiments show that most ^{226}Ra and ^{210}Pb were associated with water-insoluble (non- CaSO_4) fractions. Th, REE and Ba were found predominantly in the residual phase, which corresponds to a small fraction of the phosphate rock or monazite and to insoluble compounds such as sulphates, phosphates and silicates. It can be concluded that although all these elements were enriched in the phosphogypsum samples they were not associated with CaSO_4 itself and therefore as such pose less of a threat to the surrounding aquatic environment.

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