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# Radiochemical characterization of Brazilian phosphogypsum

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## Abstract

This work aims to determine the activity concentrations of the radionuclides in the natural series, including $^{226}$Ra, $^{210}$Pb, $^{210}$Po and the uranium and thorium isotopes, in Brazilian phosphogypsum and the ore rocks from which it is derived. The results show that $^{226}$Ra, $^{210}$Pb, $^{210}$Po and thorium isotopes fractionate preferentially to the phosphogypsum, where percentages (to ore rocks) of 90% for $^{226}$Ra, 80% for $^{232}$Th and $^{230}$Th, 100% for $^{210}$Pb and 78% for $^{210}$Po were found. The distribution of thorium isotopes seems to depend strongly upon chemical processes, since their relative concentrations in phosphogypsum (80%) were higher than expected from the available literature. The uranium isotopes are predominantly incorporated in phosphoric acid as uranyl phosphate, sulphate or fluoride complexes. The concentration ranges found for $^{226}$Ra (22–695 Bq/kg), $^{210}$Pb (47–894 Bq/kg), $^{210}$Po (53–677 Bq/kg) and $^{232}$Th (7–175 Bq/kg) in Brazilian phosphogypsum are wide but are in good agreement with results found in the literature for phosphogypsum from other locations. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Radionuclides; Uranium; Thorium; Radium; Phosphogypsum

## 1. Introduction

Phosphogypsum is the by-product of the phosphoric acid industry and is obtained by reacting phosphate rock with sulphuric acid. Approximately 69 million t of this

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by-product has already been produced by the phosphate fertilizer industry in Brazil, with a production of 5.4 million t/year. Although phosphogypsum is mainly calcium sulphate dihydrate, it contains elevated levels of impurities, which originate primarily from the phosphate rock used as raw material. All of this material is stockpiled because the impurities prevent its utilization. Relatively high concentrations of some of the uranium-series daughters, particularly $^{226}$Ra (half-life 1620 yr), prevent the use of this by-product for construction or other purposes. Long-term storage and maintenance of this material, on the other hand, presents economic as well as potential environmental concerns.

The phosphate rock used as the raw material for phosphoric acid production is enriched in uranium, thorium and their decay products. The radioactive equilibrium, however, is disrupted and a redistribution of radionuclides occurs when the phosphate rock is chemically reacted to produce phosphoric acid. The most common method of producing phosphoric acid is the so-called "wet process" in which phosphate rock is reacted with sulphuric acid. This process results in the production of substantial quantities of hydrated calcium sulphate by-products, known as phosphogypsum, according to the reaction:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4.2H_2O + 6H_3PO_4 + 2HF.$$

The commercial use of phosphogypsum in Brazil is currently limited to the production of cement, as a soil amendment and as filler in the paper industry (Damasceno & Lima, 1994). The use of phosphogypsum as a soil conditioning (substituting limestone) filler is only possible in agricultural land which is close to the fertilizer industries. In Brazil the major fertilizer industries are located in Rio Grande, in the south region of the State of Rio Grande do Sul, in Cubatão and Cajati, State of São Paulo, and in Uberaba, State of Minas Gerais.

Another possibility is to use phosphogypsum, instead of natural gypsum, as a clinker admixture in the production of cement. In this case, the amount of calcium sulphate added is roughly 5% and its main purpose is to control the setting time of the cement. This application, however, also depends upon the localization of the fertilizer industry and the cement plants to be economically feasible. Furthermore, this application could presently utilize only 10% of the total amount of phosphogypsum already available in Brazil.

Although a considerable amount of compositional data exist for phosphogypsum produced throughout the world, comparatively little detailed work had been undertaken on the re-distribution of $^{238}$U decay-series radionuclides during processing of the ores and during storage on stacks (Hull & Burnett, 1996; Rutherford, Dudas & Samek, 1994; Horton, Blanchard & Windham, 1988). In Brazil, until now, few data are available on the occurrence of natural radionuclides in phosphogypsum (Pessenda, Nascimento Filho, De Nadi & Ferraz, 1988; Godoy, 1989, Mazzilli & Saueia, 1997). This study therefore aims (1) to measure the activity concentrations of $^{226}$Ra, $^{210}$Pb, $^{210}$Po and the uranium and thorium isotopes in Brazilian phosphogypsum and the ore rocks from which it is derived; and (2) to determine the fractionation between these radionuclides during processing of the ores. The results can provide useful information for assessing public exposure to a technologically enhanced naturally occurring radioactive material (TENORM). Furthermore, regulatory measures to limit such increases may be envisaged by the national competent authorities, since there is a lack of national regulation or reference levels concerning the use or handling of this material.

## 2. Materials and methods

The phosphogypsum samples were collected from the four main producers of phosphoric acid in Brazil, named A, B, C and D. Whenever possible, samples of the raw material (phosphate rock) from which the phosphogypsum was derived were also collected. It is known that water exists in the crystalline lattice of both dihydrate and hemihydrate forms of phosphogypsum and there exist differences of up to 15.7% between the formula weights. Therefore, in order to obtain reliable results, the method by which the samples were dried and homogenized was extremely important, since all the radiochemical analysis performed are based upon gravimetric determinations. All the phosphogypsum samples studied were, therefore, prepared by drying at a temperature not greater than 45°C to constant mass, ground to a grain size of less than 250 μm and finally stored in a desiccator at room temperature. It was observed using X-ray diffraction that the predominant crystalline phase is the dihydrate form. The phosphate rock was treated in the same way as the phosphogypsum samples.

Activity concentrations of $^{232}$Th, $^{226}$Ra and $^{40}$K were measured in eight samples of phosphate rock and 10 samples of phosphogypsum by gamma-spectrometry with a hyper-pure germanium detector, GEM-15200, from EG & G Ōrtec. Each sample was analysed in duplicate. The detector was calibrated using natural soil and rock spiked with radionuclides certified by Amersham. Samples were packed in 100 cm$^3$ cans and sealed for about four weeks prior to the measurement in order to ensure that equilibrium had 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 three separate photopeaks of its daughter nuclides: $^{214}$Pb at 295 and 352 keV, and $^{214}$Bi at 609 keV. The $^{232}$Th content of the samples was determined by measuring the intensities of the 911 and 968 keV gamma-ray peaks from $^{228}$Ac. The potassium content was determined from the 1460 keV gamma-ray peak of $^{40}$K. In order to verify if $^{232}$Th was in equilibrium with its daughters in phosphogypsum, the same samples were also measured by alpha-spectrometry. The results obtained from the two techniques, presented in Fig. 1, showed that both methodologies gave representative results over the range of activities investigated.

Typical lower limits of detection for gamma-spectrometry were 0.17 Bq/kg for $^{226}$Ra, 0.59 Bq/kg for $^{232}$Th and 4.2 Bq/kg for $^{40}$K, for a counting time of 50,000 s.

The concentration of $^{210}$Pb was determined by measuring the activity of its low-energy peak (47 keV) in homogenized samples of phosphate rock and phosphogypsum in a coaxial germanium detector, EGNC 15-190-R, from Eurisys. Samples were packed in 100 $\mathrm{cm}^3$ cans and counted for 50,000 s. Self-absorption correction was applied since the attenuation for low-energy gamma-rays is highly dependent upon sample composition. The approach used was modified from that suggested by Cutshall, Larsen and Olsen (1983). According to them, the self-absorption equation may be written as

$$A/O = \frac{\ln(T/I)}{(T/I - 1)},$$

where $O$ is the attenuated sample output (count rate), $A$ is the actual sample photon emission rate, $T$ and $I$ are the attenuated and unattenuated beam intensities. The attenuated beam intensity ($T$) is defined as the difference between the count rate of each sample with and without an external source containing $^{210}$Pb centred on top of the sample container. Factor $I$ was determined by making a measurement with the same external $^{210}$Pb source placed on top of the efficiency standard. This ratio thus represents how each sample compares to the efficiency standard in terms of self-absorption. The final $^{210}$Pb activities are then obtained by substituting the relative absorption factor into the activity calculation equation, as follows:

$$A\ (\mathrm{Bq/kg}) = \frac{(C - C_0)f_{\mathrm{abs}}}{W_t \eta T \gamma},$$

where $A$ is the sample activity, $C$ and $C_0$ are the sample and background counts, $W_t$ is the sample weight in kg, $f_{\mathrm{abs}}$ is the relative absorption factor, $\eta$ is the efficiency in cps/dps, $T$ is the counting time in seconds and $\gamma$ is the peak intensity.

The lower limit of detection obtained for $^{210}$Pb was 20.6 Bq/kg, for a counting time of 50,000 s.

Radiochemical separation and alpha-spectrometry were used to determine the activities of $^{238}$U, $^{234}$U, $^{230}$Th, $^{232}$Th and $^{210}$Po in the phosphogypsum and phosphate rock samples. The procedure adopted for this analysis is modified from that of Raya (1995) and described in more detail in Saueia (1998) and Paes (1999). Accurately weighed 250–500 mg samples were dissolved in 10 ml of concentrated $HNO_3$ and a volume of 0.5 ml of each $^{208}$Po, $^{232}$U and $^{229}$Th solutions were added as tracers. To allow for complete dissolution of the sample, the solution was heated, avoiding temperatures exceeding 80°C in order to prevent losses of polonium by volatilization, and were digested with 10 ml concentrated HF and 10 ml aqua regia. The solution was then evaporated to near-dryness three times with $HNO_3$, in order to remove excess HF. The U and Th isotopes were separated from the polonium by solvent extraction using TBP (tributylphosphate). The polonium present in the aqueous phase was dried and redissolved in 20 ml concentrated HCl and 100 mg ascorbic acid. The polonium alpha-spectrometry source was then prepared by spontaneously plating the Po isotopes from an acid solution on to a copper disc (Saueia, 1998).

Xylene was added to the organic phase and U and Th were then back-extracted with water. This solution was evaporated to dryness and the residue was redissolved in 9 M hydrochloric acid. The solution was passed through an ion exchange column filled with Dowex 1 × 8 (100–200 mesh) resin. Uranium is absorbed in the column,

Table 1
Ra-226, Th-232 K-40 and Pb-210 activity concentrations (Bq/kg$^{-1}$) obtained by gamma-spectrometry in phosphogypsum and phosphate rock

| | Ra-226 | Th-232 | K-40 | Pb-210 |
|---|---|---|---|---|
| Phosphogypsum from producer A (3) | | | | |
| Mean ± stand.dev. | 695 ± 47 | 175 ± 23 | 25 ± 13 | 894 ± 210 |
| Range | 642–729 | 148–190 | 12–39 | 687–1107 |
| Phosphate rock from producer A (2) | | | | |
| Mean ± stand.dev. | 1121 ± 459 | 245 ± 35 | 24 ± 4 | 1477 ± 534 |
| Range | 796–1445 | 220–270 | 21–27 | 1099–1855 |
| Phosphogypsum from producer B (3) | | | | |
| Mean ± stand.dev. | 100 ± 7 | 156 ± 38 | 24 ± 16 | 116 ± 20 |
| Range | 93–107 | 129–200 | < 4.2–35 | 101–139 |
| Phosphate rock from producer B (3) | | | | |
| Mean ± stand.dev. | 140 ± 10 | 256 ± 81 | 29 ± 10 | 240 ± 48 |
| Range | 130–150 | 197–349 | 21–41 | 185–276 |
| Phosphogypsum from producer C (3) | | | | |
| Mean ± stand.dev. | 266 ± 21 | 174 ± 17 | 18 ± 1 | 275 ± 30 |
| Range | 249–289 | 155–188 | < 4.2–18 | 241–295 |
| Phosphate rock from producer C (3) | | | | |
| Mean ± stand.dev. | 407 ± 12 | 244 ± 40 | 18 ± 11 | 510 ± 105 |
| Range | 393–415 | 203–282 | 4.8–25 | 432–630 |
| Phosphogypsum from producer D (1) | | | | |
| | 22 ± 0 | 7 ± 1 | < 4.2 | 47 ± 9 |

*Note:* (*n*) = number of measured samples.

whereas thorium is found in the eluate. The uranium absorbed in the column was eluted by passing 0.5 M hydrochloric acid through the column. The solutions containing U and Th, separately, were dried and redissolved in sulphuric acid. Uranium and thorium were plated on stainless-steel discs by electrodeposition, using a solution of $H_2SO_4/Na_2SO_4$ (pH$\cong$3) and applying a current of 1.2 A (Paes, 1999).

Alpha-spectrometry was performed using a surface barrier detector. The efficiency of the detector (20%) was obtained by measuring an $^{241}$Am standard source from Amershan ($3.06 \times 10^5$ dpm, with an uncertainty of 2%). Typical lower limits of detection for this methodology were: 1.7 mBq/kg for $^{238}$U, 2.3 mBq/kg for $^{234}$U, 1.7 mBq/kg for $^{232}$Th, 3.3 mBq/kg for $^{230}$Th, 4.6 mBq/kg for $^{228}$Th and 3.6 mBq/kg for $^{210}$Po, for a counting time of 60,000 s. The methodology was checked experimentally by measuring uranium, thorium and polonium in the reference materials stream sediment (IAEA-313) and Baltic sea sediment (IAEA-300). The reproducibility was characterized by average variation coefficient values of 2.5%, with an accuracy of 1.0%, for uranium, of 8.8 and 13.5%, respectively, for thorium and of 8.6 and 3.3%, respectively, for $^{210}$Po. Uranium and thorium recoveries ranged between 20 and 84%, while slightly higher values were obtained for Po (31–78%).

Table 2
U-238, U-234, Th-230, Th-232, Th-228 and Po-210 activity concentrations (Bq/kg) obtained by alpha-spectrometry in phosphogypsum and phosphate rock

| | U-238 | U-234 | Th-230 | Th-232 | Th-228 | Po-210 |
|---|---|---|---|---|---|---|
| Phosphogypsum from producer A (3) | | | | | | |
| Mean ± stand.dev. | 42 ± 6 | 48 ± 8 | 560 ± 149 | 148 ± 28 | 135 ± 35 | 677 ± 130 |
| Range | 35–47 | 38–54 | 450–729 | 129–180 | 108–174 | 541–801 |
| Phosphate rock from producer A (2) | | | | | | |
| Mean ± stand.dev. | 1128 ± 498 | 1274 ± 617 | 1206 ± 501 | 273 ± 47 | 255 ± 58 | 1472 ± 378 |
| Range | 776–1480 | 838–1710 | 852–1560 | 240–306 | 214–296 | 1205–1739 |
| Phosphogypsum from producer B (3) | | | | | | |
| Mean ± stand.dev. | 17 ± 5 | 22 ± 8 | 123 ± 73 | 94 ± 67 | 97 ± 64 | 124 ± 9 |
| Range | 13–22 | 17–31 | 47–193 | 54–171 | 47–169 | 115–134 |
| Phosphate rock from producer B (3) | | | | | | |
| Mean ± stand.dev. | 164 ± 20 | 178 ± 24 | 222 ± 47 | 286 ± 99 | 282 ± 159 | 213 ± 43 |
| Range | 148–187 | 158–205 | 184–274 | 200–394 | 123–441 | 180–262 |
| Phosphogypsum from producer C (3) | | | | | | |
| Mean ± stand.dev. | 41 ± 24 | 46 ± 25 | 310 ± 32 | 182 ± 23 | 200 ± 14 | 303 ± 35 |
| Range | 23–68 | 26–74 | 273–329 | 159–205 | 184–209 | 280–344 |
| Phosphate rock from producer C (3) | | | | | | |
| Mean ± stand.dev. | 434 ± 69 | 478 ± 79 | 527 ± 44 | 300 ± 46 | 282 ± 42 | 672 ± 97 |
| Range | 355–485 | 388–538 | 476–556 | 250–340 | 233–310 | 606–781 |
| Phosphogypsum from producer D (1) | | | | | | |
| | 11 ± 2 | 13 ± 1 | 15 ± 1 | 7 ± 1 | 20 ± 2 | 53 ± 1 |

*Note:* ($n$) = number of measured samples.

## 3. Results and conclusions

Measurements of activity concentrations for $^{226}$Ra, $^{232}$Th, $^{210}$Pb and $^{40}$K in phosphogypsum and phosphate rock, obtained by gamma-spectrometry, are summarized in Table 1. The concentrations of $^{226}$Ra, $^{232}$Th and $^{210}$Pb varied over a wide range depending upon the producer considered, while concentrations of $^{40}$K were quite similar and close to the detection limits of the equipment (4.2 Bq/kg). Phosphate rock and phosphogypsum from producer A showed the highest concentrations of $^{226}$Ra and $^{210}$Pb, while the lowest values were observed for producer D, values for which were similar to natural gypsum. The results obtained for $^{232}$Th are quite similar for producers A, B and C. Taking into account the average value for each producer, the activity concentration range for $^{226}$Ra (22–695 Bq/kg) and $^{232}$Th (7–175 Bq/kg) in the Brazilian phosphogypsum shows that the variations, although significant, are in good agreement with data published in the literature for phosphogypsum (Zikovsky & Kennedy, 1992; Rutherford et al., 1994; Othman & Mahrouka, 1994; Hull & Burnett, 1996). Some samples of phosphoric acid were also measured by gamma-spectrometry and the results obtained for $^{226}$Ra, $^{232}$Th, $^{210}$Pb and $^{40}$K were always below or close to the detection limits.

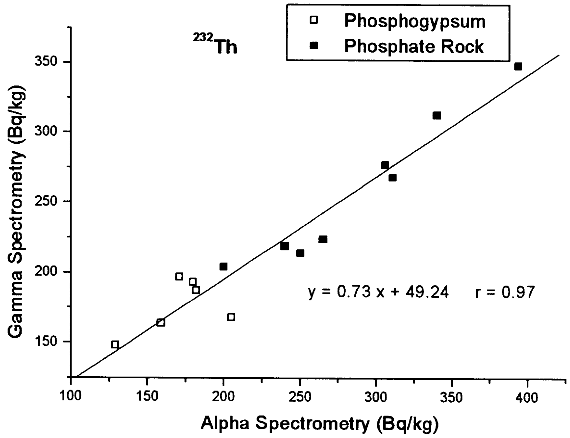

Fig. 1. Plot of $^{232}$Th activities measured by gamma-spectrometry vs. alpha-spectrometry.

The results for the activity concentrations of $^{210}$Po and uranium and thorium isotopes in phosphogypsum and phosphate rock, obtained by alpha-spectrometry, are presented in Table 2. The results obtained for $^{210}$Po in phosphogypsum varied from 53 to 677 Bq/kg. Producer A presented activity concentrations of $^{210}$Po in phosphate rock and phosphogypsum similar to those found in Florida (Hull & Burnett, 1996) and in Senegal, Morocco and Congo (Bolívar, García-Tenório & García-Léon, 1995). All the phosphogypsum samples collected in this study have activity concentrations of $^{210}$Pb and $^{210}$Po that are generally comparable to $^{226}$Ra. Analyses of U and Th isotopes in Brazilian phosphate rock and phosphogypsum show that most of the U probably fractionates to the acid phase, whereas Th is largely incorporated with phosphogypsum.

The activities of $^{232}$Th in phosphogypsum and phosphate rock have been analysed using alpha- and gamma-spectrometry and the results from the two techniques are compared in Fig. 1. The relatively good correlation coefficient of 0.97 and the slope of the line regressed through the data indicate that both methodologies gave representative results over the range of activities investigated. Some scatter in samples plotted in Fig. 1 may result from using limited quantities of samples (250–500 mg) for alpha-spectrometry and these may not be sufficiently homogenous to be representative of the 100 g samples which were measured by gamma-spectrometry.

The results in Tables 1 and 2 confirm that the various members of the $^{238}$U series decay chain, including $^{238}$U, $^{230}$Th, $^{226}$Ra, $^{210}$Pb and $^{210}$Po, are in approximate radioactive equilibrium in phosphate rock. It is clear that this equilibrium is significantly disrupted during the chemical processing of phosphate rock. This disruption is clearly shown in Fig. 2, where $^{238}$U, $^{232}$Th, $^{230}$Th, $^{226}$Ra, $^{210}$Pb and $^{210}$Po in phosphogypsum samples are plotted versus activities in the corresponding phosphate rock. A good correlation is observed. If the phosphate rock : gypsum mass ratio of 1 : 1.7 is taken into account, the slopes of the regression lines presented in Fig. 2 can give the percentage of the nuclide that fractionates to phosphogypsum. The results

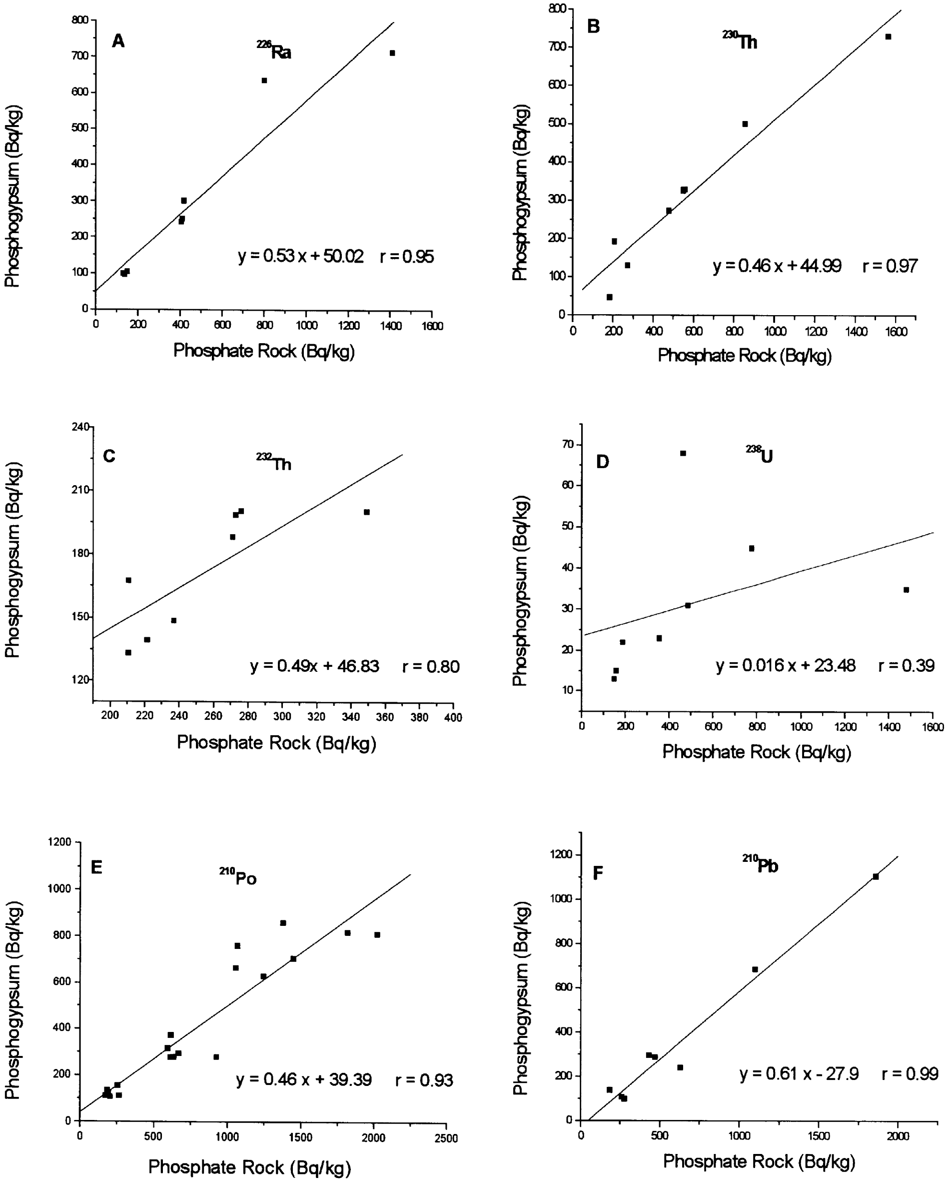

Fig. 2. Relationships of the activities of natural radionuclides in phosphogypsum vs. those in phosphate rock for (A) $^{226}$Ra, (B) $^{230}$Th, (C) $^{232}$Th, (D) $^{238}$U, (E) $^{210}$Po and (F) $^{210}$Pb.

obtained by smoothing the data in this way indicate that 100% of the $^{210}$Pb, 90% of the $^{226}$Ra, 80% of the $^{232}$Th plus $^{230}$Th, and 78% of the $^{210}$Po, fractionate to phosphogypsum. These percentages are approximate and are influenced by the non-ideal acidification reaction and unreacted phases in the phosphate rocks.

Radium is incorporated in the phosphogypsum due to its chemical behaviour being similar to calcium. Roessler (1990) suggests that radium coprecipitates as some unknown phase with $CaSO_4.nH_2O$. Other authors (Rutherford, Dudas & Arocena, 1995) propose that radium is incorporated in radiobarite (Ra-bearing $BaSO_4$) or $(Ba,Sr)SO_4$ solid phase. The results for $^{232}$Th, $^{210}$Pb and $^{210}$Po obtained in the present paper demonstrate that virtually all $^{210}$Pb and to a lesser extent $^{232}$Th and $^{210}$Po are also present in the phosphogypsum. Other authors (Hull & Burnett, 1996) have also reported the same behaviour for $^{210}$Pb and $^{210}$Po. Therefore, the extent of incorporation of these radionuclides into phosphogypsum is primarily controlled by the amount supplied by the ore rock as well as by the acidification process efficiency.

The partitioning of $^{232}$Th and $^{238}$U, on the other hand, seem to be more variable. The slopes of Fig. 2(B) and (C) indicate that about 80% of the Th is fractionated to phosphogypsum. Hull and Burnett (1996) found no correlation between the concentrations of U and Th in the phosphogypsum and the phosphate rock. The redistribution of these nuclides during acidification of phosphate rock may be controlled by a number of factors including redox potential, digestion temperature during the processing of the rock, sorption of humic substances and clays and coprecipitation with fluorides. The slope of Fig. 2(D) indicates that the $^{238}$U content of phosphogypsum shows no significant correlation with the $^{238}$U content of the phosphate rock. Any $U^{4+}$, which is in the phosphate rock, is probably oxidized to $U^{6+}$ during the acidification process and that dissolved uranium is largely incorporated in the acid phase as uranyl phosphate, sulphate and fluoride complexes.

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