

# Study of the dynamic lixiviation of $^{226}\text{Ra}$ from phosphogypsum by an automatic system previous radiometric detection

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## Abstract

The phosphogypsum (PG) is a by-product from phosphate fertilizer industry, it is produced in large amount, and contains naturally radionuclides, principally  $^{226}\text{Ra}$  and these decay products. The lixiviation study of the radionuclides from PG has great industrial and environmental importance due to the reutilization possibilities. A study of dynamic lixiviation of  $^{226}\text{Ra}$  in PG samples was carried out with an automatic system composed by a lab-on-valve and multisyringe flow injection analysis. Artificial rainwater at two different pH ( $5.4\pm 0.2$  and  $2.0\pm 0.2$ ), was used as leaching agent. The PG sample was placed in a designed column, and the leaching agent passed through the column at a flow rate of  $3.5 \text{ mL min}^{-1}$ . Eight leaching fractions of 30 mL each one were recollected. Each leaching fraction was analyzed in an automatic system for the extraction/pre-concentration of  $^{226}\text{Ra}$ , which is absorbed on manganese dioxide formed on cellulose beads. Then,  $^{226}\text{Ra}$  is eluted with hydroxylamine and finally co-precipitated with barium sulfate. The  $^{226}\text{Ra}$  activity was measured with a low background proportional counter. The specific activities of the leaching are between 28 and 12  $\text{Bq Kg}^{-1}$  from artificial rainwater at pH 2, and in the range of 16 and 10  $\text{Bq Kg}^{-1}$  at pH 5.4. The sum of eight fractions reached up to 52% of the total  $^{226}\text{Ra}$  content in the PG sample, which is to highlight considering that re-absorption processes not occur in dynamic lixiviation. This methodology was validated by analyzing a PG reference material (MatControl CSN-CIEMAT 2008).

## Introduction

The phosphogypsum (PG) is produced in large amount through acid phosphoric production by the wet process (Aguado et al., 2005; Haridasan et al., 2002). The PG contains natural radionuclides, mainly  $^{226}\text{Ra}$  and its decay products (Al-Hwaiti et al., 2010; Gázquez et al., 2009). After the wet process, between 80-90% originally present in phosphate rock stays in PG (Aguado et al., 2005; Bolívar et al., 1998; EPA, 1992). Much of the PG produced is stored in stockpiles exposed to meteorological process (Villa et al., 2009) causing damage to the environment.  $^{226}\text{Ra}$  is alpha emitter with a long half-life (1600 y), that increase its environmental control (Atwood, 2010).  $^{226}\text{Ra}$  activity in PG varies if the sample is collected in different basins within the same geographic area and if collected at different points within the same raft (EPA, 1992). The study of radionuclide leaching from PG is of great environmental and industrial importance because of their reusability. The leaching of  $^{226}\text{Ra}$  from PG has been studied mainly in a static approach, i.e. using a large amount of sample and leaching agent, and maintaining the contact time between the sample and the leaching agent for a long time (Aguado and Bolívar, 1999; Aguado et al., 2005; Azouazi et al., 2001; Haridasan et al., 2002; May and Sweeney, 1984). The conventional method of lixiviation has some limitations, including the  $^{226}\text{Ra}$  reabsorption which can be up to 89% of the leaching content (May and Sweeney, 1984). To solve these inconvenient, a dynamic lixiviation of  $^{226}\text{Ra}$  exploiting flow

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analysis techniques is proposed. Continuous leaching agent flow through the sample allows the constant renewal of leaching agent, disfavoring the reabsorption process by continuously varying the equilibrium liquid-solid (Bacon and Davidson, 2008). The combination of the multisyringe flow technique analysis (MSFIA) (Cerdà et al., 1999) and lab-on-valve (LOV) (Ruzicka, 2000) combines the advantages of both techniques in one system. The main objective of this work is the evaluation of dynamic leaching of  $^{226}\text{Ra}$  in PG samples, using artificial rainwater as leaching agent by an automatic system (MSFIA-LOV) previous radiometric detection.

## Materials and Methods

### *Samples*

PG samples were obtained from inactive deposits from Fertiberia in Huelva, Spain. The PG reference sample material MatControl CSN-CIEMAT 2008 was used to validate the proposed methodology. The samples were dried at  $55\pm 5^\circ\text{C}$ , until constant weight. The digestion of the PG samples and the residual fraction was carried out with 10 mL of  $\text{HNO}_3$  (69%) in a microwave (Multiwave Go, Anton Paar) following the EPA 3052 method. After the digestion process, the  $\text{HNO}_3$  concentrated was evaporated to dryness and the residual was diluted in 25 mL with Milli-Q water, finally the solution was filtered through a  $0.45\ \mu\text{m}$  filter and the pH was adjusted to  $7.0\pm 0.5$ .

### *Analytical procedure*

The leaching, extraction and pre-concentration of  $^{226}\text{Ra}$  was carried out with an MSFIA-LOV system presented in Figure 1.

- 1) PG sample was placed in the leaching column and 30 mL of artificial rainwater passed through the column.  $0.22\ \text{mol L}^{-1}\text{NaOH}$  was dispensed to the PG leaching recollect, adjusting the pH at  $7.0\pm 0.5$ . The leaching was stirred for its homogenization.
- 2) Macroporous bead cellulose (MBC) column (port 8) was conditioned with hot deionized water ( $70^\circ\text{C}$ ). Subsequently,  $\text{KMnO}_4$  was dispensed on MBC column, keeping the contact for 2 min to help the formation of  $\text{MnO}_2$ . The sample was loaded into the MBC column at  $1.5\ \text{mL min}^{-1}$ .
- 3) Elution of  $^{226}\text{Ra}$  was performed by dispensing  $\text{NH}_2\text{OH}\cdot\text{HCl}$  through the MBC column. Then,  $^{226}\text{Ra}$  was co-precipitated with  $\text{Na}_2\text{SO}_4$  and acetate/ $\text{Ba}^{+2}$  buffer. A wait of 30 minutes was necessary for the formation of  $\text{Ba}(\text{Ra})\text{SO}_4$ .
- 4) The MBC column was automatically regenerated replacing the old beads by new ones, which are on the reservoir (port 4) in 20:80 methanol:water (v/v).
- 5) Finally,  $^{226}\text{Ra}$  co-precipitated formed was filtered through a  $0.22\ \mu\text{m}$  nylon filter and was dried to dryness on a steel planchette under the infrared lamp. The alpha activity of each sample was determined in a low background proportional counter Canberra LB4200.

## Results and Discussion

### *Optimization of the experimental conditions*

The optimization of the PG leaching variables were studied by a multivariate approach. The independent factors were: PG sample weight and the leaching flow rate. A full factorial design  $2^2$  was performed into the range 200-600 mg of sample and  $2 - 5\ \text{mL min}^{-1}$  flow rate. The range of the sample weight was according to the quantity of PG packed into the cell, without causing an impediment in the flow during the leaching process. The results (ANOVA table, Pareto chart) indicate that variables have not shown significant effects into the experimental domain studied, with 95% of confidence level. The central point of assays ( $0.400\ \text{mg}$  and  $3.5\ \text{mL min}^{-1}$ ) were used in further assays, since the results shown the lower RSD.

The optimal pH value of the sample, e.g. leached fraction, residual fraction and entire sample, to introduce in the extraction/pre-concentration manifold was studied between pH 6 – 8. The best

results were obtained between pH 6.5 to 7.5. The automatic system for extraction and pre-concentration of  $^{226}\text{Ra}$  had been previously optimized (Rodríguez et al., 2016).

#### *Validation of the method*

The validation of the method was performed with a PG reference sample material (MatControl CSN-CIEMAT 2008). Eight fractions of 30 mL of artificial rainwater at pH  $2.0\pm 0.2$  were analyzed. After the lixiviation process, the residual fraction was dried at  $55\pm 5^\circ\text{C}$  until constant weight. Finally, the digestion process was performed on the residual fraction and total sample. The results were validated with the z-score value, being satisfactory with a z-score less than 2 (Table 1).

#### *$^{226}\text{Ra}$ dynamic lixiviation in PG samples*

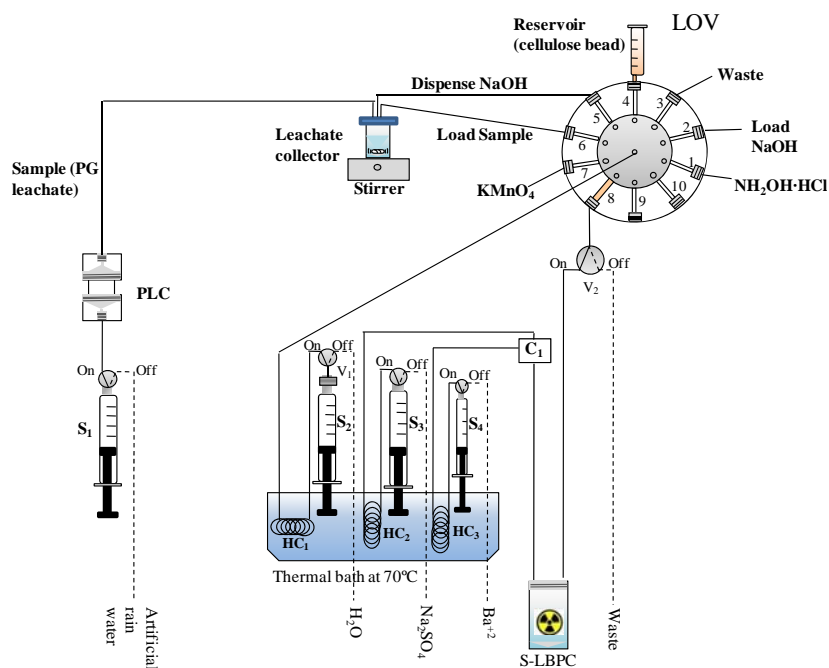
The studied of the dynamic leaching of  $^{226}\text{Ra}$  was carried out with artificial rainwater at pH  $5.4\pm 0.2$  as leaching agent, and also with a pH  $2.0\pm 0.2$  in order to study the behavior of the radium release in an acid medium (Table 2). Eight leaching fractions were analyzed, because the ninth fraction overlapped with the minimum detectable activity (MDA,  $7 \text{ Bq Kg}^{-1}$ ) (Figure 2). Using artificial rainwater at pH 5.4, the released  $^{226}\text{Ra}$  reached 37%, which is higher than those obtained in static studies. Between 0.24–16% of the  $^{226}\text{Ra}$  total content in PG sample was lixiviated in static conditions (Aguado and Bolívar, 1999; Aguado et al., 2005). A 24% of lixiviation was the higher release achieved with 24 h contact time (Haridasan et al., 2002). For assays with artificial rainwater at pH 2.0, the released  $^{226}\text{Ra}$  reached up to 50% of the total content in PG sample. These higher  $^{226}\text{Ra}$  contents in the leached fractions, both in the dynamic vs. static processes and using a more acidic extractant, are due to direct dependence on the leaching conditions such as pH of the extractant and the contact time between sample and extractant (Haridasan et al., 2002). In this sense, in the dynamic approach, the contact time between the sample and the extractant is given by the lixiviation flow rate used. In this work, taking into account the cell capacity and the flow rate of  $3.5 \text{ ml min}^{-1}$ , the contact time is of 9 min since the agent enters the cell until it leaves. Thus, it can be considered that the leaching agent is renewed constantly and the equilibrium is displaced to benefit the extraction. In addition to the leaching process itself,  $^{226}\text{Ra}$  determined in each fraction partially comes from the dissolution of PG. In order to quantify such contribution, the remanent sample together with the filters that help to contain it into the cell, were dried in oven at  $55^\circ\text{C}$  up to constant weight after each lixiviation cycle, and weighted. Results indicate that PG solubility reaches between 18–20%, in accordance with previously reported values (Aguado et al., 2005; Haridasan et al., 2002; Rutherford, P. M., Dudas, M. J., Arocena, 1995).

#### **Conclusions**

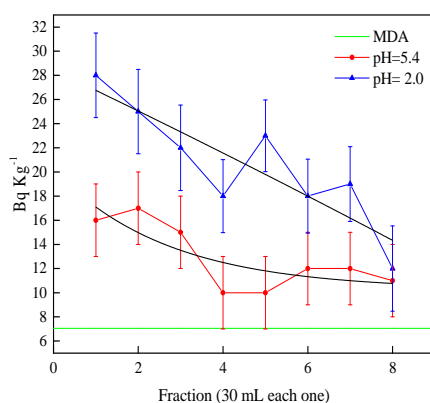
- A dynamic lixiviation of  $^{226}\text{Ra}$  was carry out in PG samples through an automatic system, including the lixiviation, and extraction/pre-concentration steps.
- Up to 37% of the total of  $^{226}\text{Ra}$  was leached using artificial rainwater as leaching agent at pH 5.4. Meanwhile, a 50% of the total content of  $^{226}\text{Ra}$  present in the PG samples was leached at pH 2.0.
- Dynamic leaching avoids reabsorption process of  $^{226}\text{Ra}$  in the PG.
- Between an 18-20% of PG is dissolved at the end of the leaching process.

#### **Acknowledgements**

Financial support from the Spanish Ministry of Economy and Competitiveness (MINECO) (CTM2013-42401-R) cofinanced by European Regional Development's funds (FEDER), are gratefully acknowledged. M. Rodas acknowledges MINECO for the allowance of an Industrial PhD fellowship (DI-14-06961).



**Figure 1.** Automatic system for the dynamic leaching, extraction/ pre-concentration and co-precipitation of  $^{226}\text{Ra}$  from PG samples. C: Three-way connector, HC: holding coil, LOV: Lab-on-valve; MSFIA: multisyringe module, PLC: phosphogypsum lixiviation column, S: syringe, V: external solenoid valve.



**Figure 2.**  $^{226}\text{Ra}$  specific activity for leached fractions with artificial rainwater. The results are expressed as weighted average  $\pm$  uncertainty ( $n=3$ ).

**Table 1.** Validation results of reference PG material (MatControl CSN-CIEMAT 2008).

	Specific activity ( $\text{Bq Kg}^{-1}\text{d.w.}$ )	$^{226}\text{Ra}$ (%)	Z-score
$\sum_{F=1}^8 F$ (sum of leached fractions)	$295 \pm 14$	52	
Residual fraction	$276 \pm 13$	48	
Sum of fractions (leached+ residual)	$571 \pm 14$	100	-0.03
Total digestion	$585 \pm 8$		0.13
Reference value	$573 \pm 115$		--

**Table 2.** Specific activity of  $^{226}\text{Ra}$  in the leached fractions and the residual fraction in samples of phosphogypsum, using artificial rainwater as extracting agent at pH 5.4 and 2.0.

	pH5.4±0.2		pH2.0±0.2	
	Specific activity (Bq Kg <sup>-1</sup> d.w.)	<sup>226</sup> Ra (%)	Specific activity (Bq Kg <sup>-1</sup> d.w.)	<sup>226</sup> Ra (%)
Fraction 1	16±3	6	28±4	9
Fraction 2	17±3	6	25±3	7
Fraction 3	15±3	5	22±3	5
Fraction 4	10±3	4	18±3	5
Fraction 5	10±3	4	23±3	9
Fraction 6	12±3	4	18±3	6
Fraction 7	12±3	4	19±3	4
Fraction 8	11±3	4	12±3	3
Σ <sub>F=1</sub> <sup>8</sup> F (sum of leached fractions)	104±3	37	166±3	50
Residual fraction	177±36	63	163±18	50
Sum of fractions (leached+ residual)	280±25	100	329±13	100

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