Short communication

Changes in mobility of toxic elements during the production of phosphoric acid in the fertilizer industry of Huelva (SW Spain) and environmental impact of phosphogypsum wastes

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Abstract

Presently, about 3 million tonnes of phosphogypsum are being generated annually in Spain as by-product from phosphoric acid in a fertilizer factory located in Huelva (southwestern Iberian Peninsula). Phosphate rock from Morocco is used as raw material in this process. Phosphogypsum wastes are stored in a stack containing 100 Mt (approximately 1200 ha of surface) over salt marshes of an estuary formed by the confluence of the Tinto and Odiel rivers, less than 1 km away from the city centre. A very low proportion of this waste is used to improve fertility of agricultural soils in the area of the Guadalquivir river valley (Seville, SW Spain). The chemical speciation of potentially toxic elements (Ba, Cd, Cu, Ni, Sr, U and Zn) in phosphogypsum and phosphate rock was performed using the modified BCR-sequential extraction procedure, as described by the European Community Bureau of Reference (1999). This study has been done with the main of: (1) evaluate changes in the mobility of metals during the production of phosphoric acid; (2) estimate the amount of mobile metals that can affect the environmental surrounding; and (3) verify the environmentally safe use of phosphogypsum as an amendment to agricultural soils. The main environmental concern associated to phosphoric acid production is that Uranium, a radiotoxic element, is transferred from the non-mobile fraction in the phosphate rock to the bioavailable fraction in phosphogypsum in a rate of 23%. Around 21% of Ba, 6% of Cu and Sr, 5% of Cd and Ni, and 2% of Zn are also contained in the water-soluble phase of the final waste. Considering the total mass of phosphogypsum, the amount of metals easily soluble in water is approximately 6178, 3089, 1931, 579, 232, 193 and 77 t for Sr, U, Ba, Zn, Ni, Cu and Cd, respectively. This gives an idea of the pollution potential of this waste.
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1. Introduction

Phosphate fertilizer for agriculture is obtained by phosphate rock wet chemical treatment with sulphuric acid. In this process, not only the commercial phosphoric acid is produced but also an insoluble residual calcium sulphate called phosphogypsum (Eq. (1)). Phosphogypsum is a by-product composed mainly by a gypsum matrix ($CaSO_4 \cdot 2H_2O$) with high contents of impurities such as P_2O_5, F, organic substances, potentially toxic metals and radioactive elements [1].

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O$$
$$\rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF \qquad (1)$$
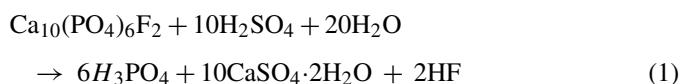
About 5 t of phosphogypsum are generated for every tonne of phosphoric acid manufactured. At present, worldwide production of phosphogypsum is over 100–280 Mt/year [2]. This low-cost waste is usually used as a fertilizer in agriculture, as a building material and as amendment for soil stabilization [3–5]. Nevertheless, such practices are limited by the high content of toxic impurities for human health, and only 15% of the worldwide production is recycled. The remaining 85% requires big disposal surfaces and causes huge environmental problems [6].

In Spain, the production of phosphoric acid, and hence of phosphogypsum, is restricted to a fertilizer industrial site in the town of Huelva (SW Iberian Peninsula). This large complex is located at the confluence of the Tinto and Odiel rivers, an estuarine zone of salt marshes with high ecological value (Fig. 1). Over 3 Mt of phosphogypsum wastes are produced each year and deposited in a stack occupying a large part of the salt marshes
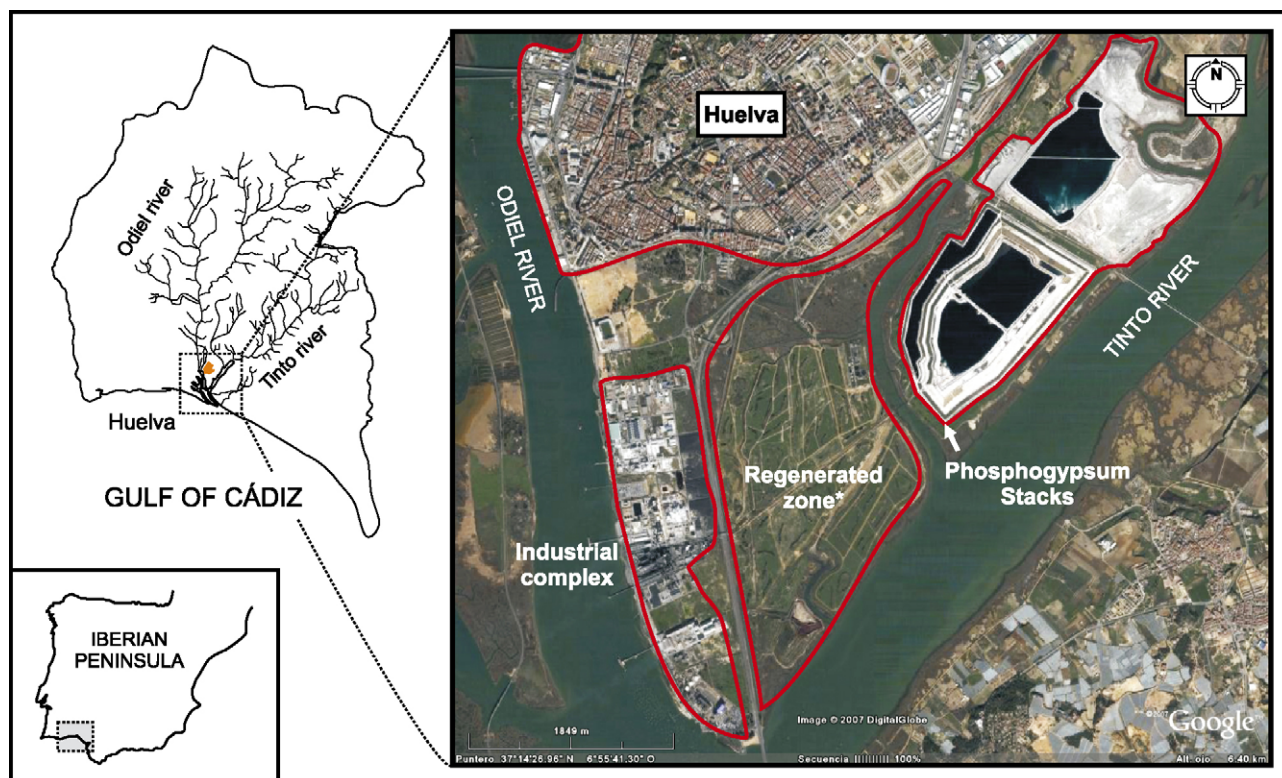

Fig. 1. Location map of the phosphogypsum pile next to Huelva town (SW Spain). The Atlantic Ocean is approximately 10 km to the south of confluence between Odiel and Tinto rivers. (*) Regenerated zone: a soil cover of 30 cm and a vegetal coverage were added above the naked phosphogypsum surface. Image from Google Earth[©] software.

associated to the right margin of the Tinto river, located less than 1 km away from the city centre. Until 1998, around 20% of the waste produced was also poured directly into the Odiel river. This dump (1200 ha of surface and 5 m of average height) contains about 100 Mt of phosphogypsum, which have caused an important environmental and ecological deterioration of the zone. However, similar salt marshes but in the Odiel river margin were declared as a Biosphere Reserve by UNESCO in 1983, famous for its high ornithological diversity and for the presence of halophytic vegetation.

The radioactive impact originated by the radionuclides of the U-series contained in the phosphogypsums of Huelva is widely described in the literature [7,8]. The phosphogypsum stack, located in the tidal prism of the estuary (Fig. 1), is not totally watertight. Effluents coming from the leaching of this waste affect the water and sediments of the nearby fluvial systems by radioactivity [9] and even extend to some remote zones of the rivers as a result of the tidal action [10]. Probably, some U in this waste is associated to the easily mobile fraction but the exact rate has not been estimated yet. There are also no works establishing the hazard of phosphogypsum as a source of other non-radioactive though potentially toxic elements for human health.

The crucial point of establishing the potential hazard of phosphogypsum is to know the chemical state in which metals are bounded to this waste (i.e., water soluble fraction, oxides, organic compounds, ions in crystal lattices of minerals),

which determine their mobilization capacity and bioavailability [11,12]. The most commonly used technique to calculate the different forms of metals in for example sediments, soils, wastes is the sequential extraction procedure, whereby several reagents are used consecutively to extract operationally defined phases in a sequence. The most simple and standardized sequential extraction method was proposed by the European Community Bureau of Reference (BCR) [13] and improved in later studies [14,15].

The main objective of this study, through the applicability of the modified BCR-sequential extraction, is to estimate the speciation of Ba, Cd, Cu, Ni, Sr, U and Zn in phosphogypsums in Huelva for the evaluation of these elements mobility. This serves as a basis to assess the role of phosphogypsum as a source of contaminants to the surrounding environment and even to soils in the Guadalquivir river valley (Seville, SW Spain), where a very small proportion of this waste is used as agricultural fertilizer [16]. By means of fishing or agricultural activity, the transference of mobile metals through the food chain might also affect human health.

In Huelva, the fertilizer plant processes phosphate rock ore from Morocco. The high content of this rock in U-series radionuclides has already been well established [7]. This rock has also been used to study the mobility of U and other non-radioactive elements (Ba, Cd, Cu, Ni, Sr and Zn), which will allow us to evaluate how the phosphoric acid generation process in the production plant alters the mobility degree of the contaminants in the waste with respect to the original rock.

2. Materials and methods

2.1. Sample collection and preparation

Two types of materials were studied: (1) phosphate rock from Morocco used in the phosphoric acid processing plant; and (2) phosphogypsum waste. A representative sampling was performed in the phosphogypsum stack where samples (approximately 2 kg) were collected using a polypropylene shovel and subsequently transferred to clean polypropylene bags. In the laboratory, the waste was grounded, oven-dried (40 °C) until complete dryness, homogenized, sieved (<2 mm) and stored in polypropylene containers. Analyses were carried out soon after sampling. The data relative to two representative samples of phosphate rock and phosphogypsum are discussed in this paper.

2.2. Reagents

Double-deionized water (18.2 MΩ) was used for preparing the solutions and dilutions. Analytical grade acetic acid (Qemical©), hydroxylamine hydrochloride (Merck©), hydrogen peroxide (Panreac©), ammonium acetate (Panreac©), suprapure hydrochloric (Merck©) and nitric acids (Merck©) were used for the sequential extraction procedure. All glassware and plastic material used were previously treated in 10% (v/v) analytical grade nitric acid and rinsed with distilled water before use.

2.3. Sequential extraction method

The procedure is summarised below and full details can be found elsewhere [14,15].

2.3.1. Step 1 (water/acid soluble and exchangeable fraction)

For each sample, 40 ml of $0.11 \, \mathrm{mol \, l^{-1}}$ acetic acid was added to 1 g dry material in a 60 ml polypropylene centrifuge tube and shaken for 16 h at room temperature. The extract was separated from the solid residue by centrifugation, decanted into a polyethylene bottle and stored at 4 °C until analysis with ICP–AES (inductively coupled plasma–atomic emission spectroscopy). The residue was washed with distilled water and the washings discarded.

2.3.2. Step 2 (reducible fraction)

Forty milliliters of $0.1 \, \mathrm{mol \, l^{-1}}$ hydroxylamine hydrochloride (adjusted to pH of around 2 by adding of HNO_3) was added to the residue from Step 1 in the centrifuge tube. Again, the extraction was performed as described in Step 1.

2.3.3. Step 3 (oxidizable fraction)

Ten milliliters of $8.8 \, \mathrm{mol \, l^{-1}} \, H_2O_2$ (pH 2.0–3.0) was added carefully in small aliquots into the residue from Step 2. The tubes were covered and the contents digested for 1 h at room temperature and 1 h at 85 °C in a water bath. Then, the volume was reduced to around 2–3 ml by further heating of the uncovered tube. This step was done twice (e.g. more details in [15]). After cooling, 50 ml of $1.0 \, \mathrm{mol \, l^{-1}}$ ammonium acetate (adjusted to pH 2 by adding HNO_3) was added to the residue, which was extracted as described in Step 1.

2.3.4. Step 4 (residual fraction)

The residue from Step 3 was digested adding 10 ml of aqua regia (a mixture of $12 \, \mathrm{mol \, l^{-1}}$ HCl and $15.8 \, \mathrm{mol \, l^{-1}} \, HNO_3$ in the ratio 3:1) into Teflon reactors. Reactors allowed to stand for 20 h in a fume cupboard, and then simmered on a hot plate for 1 h at 100 °C.

The hazard of both phosphogypsum waste and phosphate rock depends directly on their capacity to easily release U and other potentially toxic metals into water. Fraction 1 consists of exchangeable metals and those soluble in water or in slightly acidic conditions. It is the fraction with the most labile bond to the samples and therefore, the most dangerous and bioavailable for the environment. Fractions 2 and 3 may also be a threat depending on the environmental conditions. Fraction 2 represents metals bound to oxides that can be released if conditions change from oxic to anoxic state. Fraction 3 is made up of metals bound to organic compounds and sulphides (the latest is not included in theses residues), which may be released under oxidizing conditions. Finally, fraction 4 corresponds to those metals strongly associated with crystalline structures of minerals, which are therefore unlikely to be released from the samples.

The sum of four fractions is equal to the total content of each element in both samples, since no undigested solid residue was left after the sequential extraction procedure. Thus, the transfer rate of elements from phosphate rock to phosphogypsum during the wet phosphoric acid process (element transfer factor, ETF) could be calculated according to the following reaction (Eq. (2)):

$$
ETF = \frac{\text{Total element concentration in phosphogypsum}}{\text{Total element concentration in phosphate rock}}
$$
$$
\times 100 \tag{2}
$$

2.4. Chemical analysis and quality control

Samples from the sequential extraction were analysed at Activation Laboratories Ltd (ACTLABS, Ontario, Canada), accredited under ISO 9001 and 9002. A total of 36 elements (Ba, Al, K, Mg, Mn, Si, Ag, As, Be, Bi, Ca, Cd, Ce, Co, Cr, Fe, Cu, Li, Mo, Na, Ni, P, Pb, Sb, S, Se, Sn, Sr, Te, Ti, Tl, U, V, W, Y and Zn) were determined by ICP–AES. To validate the results, the analysis sequence consisted of calibration standards, standard solutions analysed as unknown (quality control solutions), method blanks, replicate solutions and two certified reference solutions: riverine water (SLRS-4) from the National Research Council of Canada (NRCC) and natural water (NIST 1640) from the National Institute of Standards and Technology (Gaithersburg, USA). The most pollutant metals found on the samples (Ba, Cd, Cu, Ni, U and Zn) are discussed in this paper.

3. Results

The extracted percent values of Ba, Cd, Cu, Ni, Sr, U and Zn in both phosphate rock and phosphogypsum waste in each

Table 1
Results obtained of BCR sequential extraction analysis for phosphate rock and phosphogypsum waste – F1 (easily soluble fraction); F2 (reducible fraction); F3 (oxidizable fraction); R (residual fraction) and the total element concentration. Element transfer factors are also shown in this table

Sample	Step (%)	Elements						
		Ba	Cd	Cu	Ni	Sr	U	Zn
Phosphate rock	F1	31	7	26	5	12	0	5
	F2	19	27	0	0	9	0	2
	F3	0	0	0	0	0	0	0
	R	50	67	74	95	79	100	92
Total (mg/kg)		59	11	27	36	536	99	197
Phosphogypsum	F1	21	5	6	5	6	23	2
	F2	13	23	0	0	5	0	2
	F3	37	19	30	0	45	0	21
	R	29	52	63	95	44	77	74
Total (mg/kg)		92	15	32	43	963	135	263
Element transfer factor (%)		156	135	117	120	180	136	134

sequential extraction step with respect to the total concentration are shown in Table 1 and represented in Fig. 2. The total concentrations of elements extracted in the mobile phases (based on the sums of the first three fractions, i.e. F1 + F2 + F3) are in the following abundance order in mg/kg:

- Sr (110) > Ba (29) > Zn (15) > Cu (7) > Cd (4) > Ni (2) > U (0), for the phosphate rock;
- Sr (543) > Zn (68) > Ba (65) > U (31) > Cu (12) > Cd (7) > Ni (2), for the phosphogypsum waste.

In phosphate rock, the concentrations of metals in relative abundance in the mobile fraction are in the following order: Ba (50%) > Cd (33%) > Cu (26%) > Sr (21%) > Zn (8%) > Ni (5%) > U (0%) (Fig. 2a). This fraction concerns the bioavailable fraction (water soluble, i.e. F1) and the reducible fraction (bounded to oxides, i.e. F2), since there are no metals bounded to the oxidizable fraction (bounded to organic matter, i.e. F3). The total content of Cu and Ni from the mobile fraction is released into the bioavailable fraction, the most dangerous for

the environment. Likewise, the percentage of Ba, Sr, Cd and Zn released in the bioavailable fraction is 31, 12, 7 and 5%, respectively. There are significant contents for example Cd (27%), Ba (19%) and Sr (9%) leached in the reducible fraction (F2). The total content of U is strongly associated to crystalline structures (residual fraction, i.e. F4) and hence, is not easily released in solution.

In phosphogypsum waste, metal contents in the mobile fraction are in the following relative abundance order: Ba (71%) > Sr (56%) > Cd (48%) > Cu (37%) > Zn (26%) > U (23%) > Ni (5%) (Fig. 2b). The most potentially toxic fraction for the environment, that is, the bioavailable fraction, is composed of U (23%), Ba (21%), Cu (6%), Sr (6%), Cd (5%), Ni (5%) and Zn (2%). Thus, the total mobile content of U and Ni is leached in the bioavailable fraction. This waste shows high Cd (23%), Ba (13%) and Sr (5%) contents related to the reducible fraction, as well as very high contents of most of the metals in the oxidizable fraction (bounded to organic matter): Sr (45%) > Ba (37%) > Cu (30%) > Zn (21%) > Cd (19%). The element transfer factor is higher than 100% for all elements (Table 1).
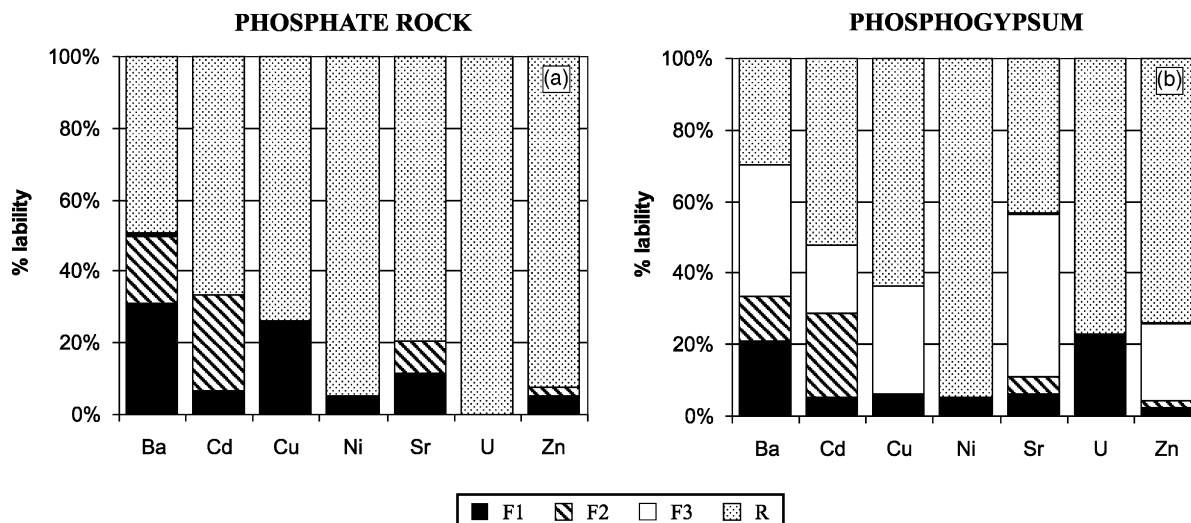

Fig. 2. Percentage of Ba, Cd, Cu, Ni, Sr, U and Zn extracted in each step of the sequential extraction procedure for (a) phosphate rock and (b) phosphogypsum waste.

Table 2
Total amount (t) of bioavailable, bounded to oxides and bounded to organic mater metals in phosphogypsum from Huelva

Phosphogypsum (100 Mt)	Elements (t)						
	Ba	Cd	Cu	Ni	Sr	U	Zn
Bioavailable fraction	1931	77	193	232	6178	3089	579
Reducible fraction	1200	300	0	0	4600	0	500
Oxidizable fraction	3379	290	965	0	43440	0	5647
Total impact	6509	667	1158	232	54219	3089	6726

4. Discussion and conclusions

Changes in mobility of toxic elements during the production of phosphoric acid by wet process in a fertilizer plant in SW Spain are discussed in this paper. The most significant changes identified are: (1) the studied metals are effectively transferred from the phosphate rock to phosphogypsum waste, as indicated by the element transfer factors (Table 1); (2) phosphogypsum displays higher relative and absolute concentrations of metals contained in the mobile fraction than phosphate rock; (3) most of these metals in phosphogypsum are bounded to organic matter (i.e. oxidizable fraction), unlike phosphate rock, that does not contain metals associated to this fraction; and (4) whereas the U of phosphate rock is associated to the non-mobile fraction, phosphogypsum contains high U concentrations bounded to the bioavailable fraction, being hence a threat for the environment.

Average element transfer factor of metals from Moroccan phosphate rock to phosphogypsum is of $140 \pm 22\%$. As a comparison, element transfer factors varied from 30 to 54% for Cd, 64 to 100% for Cu and 20 to 44% for Zn in the United States [1] and 30% for Zn, 17% for U and 8% for Cd in Syria [17]. Both in Syria and in the United States a large amount of metals are portioned into phosphoric acid. However, in Huelva all studied metals are transferred and enriched in phosphogypsum, as occurred with Brazilian phosphoric acid producers, except for U [18]. From a commercial point of view, the phosphoric acid produced in Huelva acquires a good quality but from an environmental point of view, phosphogypsum becomes a more hazardous waste than in other countries owing to higher concentrations of impurities.

The pile of phosphogypsum is exposed to weathering conditions (Fig. 1). The regional climate is of a Mediterranean type, that is, rainy winters and warm-dry summers. This means that the most potentially dangerous fractions in phosphogypsum are the bioavailable and oxidizable ones. In rainy periods, metals bounded to the bioavailable fraction, made of soluble phases in rainwater, are released into solution. Whereas in warm periods, the high porosity of these wastes [19] favours the continuous atmospheric oxygen input and the release of metals associated to organic matter (oxidizable fraction), which will be leached with the first autumn rainfalls, since the warm periods are also dry. This process is repeated and pollution is assured every year. Effluents from the leaching of phosphogypsum might present high concentrations of these metals but also particulate material and consequently "mobile". In the estuary of Huelva, the existence of reducing environments favouring the precipitation of

diagenetic pyrite is common [20], which consequently should favour the release of metals associated to oxides from the phosphogypsum particulate material (reducible fraction).

The maximum amount of mobile contaminants can be estimated taking into account the total mass of phosphogypsum (Table 2). In the hypothetical case of the stack breaking up and waste spilling to the estuary, water-soluble metals are the first to be released: 6178, 3089, 1931, 579, 232, 193 and 77 t of Sr, U, Ba, Zn, Ni, Cu and Cd, respectively. This gives an idea of the extreme contamination potential of phosphogypsum, not considering the release of metals associated to organic matter in superficial oxygenated zones and metals associated to oxides in deeper reducing zones of the estuary.

The Iberian Pyrite Belt (IPB) is also located in the Huelva province. It is one of the largest massive sulphide deposits in the world [21]. The mining activity in the IPB has produced a huge volume of sulphide-rich mining wastes and the generation of extremely acid and contaminated leachates (Acid Mine Drainage, AMD) that reach the Tinto–Odiel estuarine system from historical times [22,23]. The later authors estimated that the mean AMD-contaminants discharge in the estuary is around 7900, 5800, 3500, 1700 and 1600 t/year of Fe, Al, Zn, Cu and Mn, respectively, with minor quantities of other metals. Effluents from the phosphogypsum stack involve not only an additional contribution to the estuary of some of the metals related to AMD, but also of new contaminants (Sr, U and Ba). Uranium is the most dangerous due to its radiotoxicity. Borrego et al. [24] also showed enrichment of rare earth elements in estuarine sediments generated by effluents from phosphogypsum waste.

As the rest of metals, U is also concentrated in phosphogypsum during the production of phosphoric acid. Although both phosphate rock and phosphogypsum contain U and are consequently radioactive, this element is totally non-mobile in phosphate rock. However, 23% of U is present as water-soluble mobile phase in phosphogypsum. This amount is similar to that contained in Syrian phosphogypsum [17]. The dissolution of U-phases or transport of particulate material within effluents can affect remote zones of the estuary by radioactivity, which is congruent with the data reported by Bolivar et al. [10]. The bioavailable amount of U (and other metals) should also be considered when using this waste as an amendment to agricultural soil, as has been done in the Guadalquivir river valley.

Part of the AMD-related metals flowing into the estuary of Huelva is distributed by Atlantic coastal currents parallel to the coast, reaching even the Mediterranean Sea through the Strait of Gibraltar [25]. On 31 December 1998, a strong storm whipped

up the Huelva city and originated waves of several meters of height that collapsed one of the modules of the phosphogypsum stack and 50,000 m^3 of acid waters were spilled to the Estuary of Huelva. We concluded that in the hypothetical case of a stack total breaking up, both the bioavailable U (approximately 3100 t) and that associated to particulate material would have the same fate as mining contaminants, and therefore will be transported not only into the estuary, but also into the Gulf of Cadiz [25].

Acknowledgements

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