

Radioactive Characterization of Leachates and Efflorescences in the Neighboring Areas of a Phosphogypsum Disposal Site as a Preliminary Step before its Restoration

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Abstract

After the recent closing of some phosphoric acid plants located in the South-West of Spain, it has been decided to restore a big extension (more than sixty hectares) of salt-marshes where historically some million tonnes of phosphogypsum (PG), the main by-product generated by these plants, have been disposed of. This PG is characterized for containing high activity concentrations of several radionuclides from the uranium series, mainly ²²⁶Ra, ²¹⁰Pb and ²¹⁰Po and to a lesser extent U-isotopes.

The PG disposal area can be considered as a potential source of radionuclides to their nearby environment, through the waters which percolate from them and through the efflorescences formed in their surroundings. A previous detailed radioactive characterization of the mentioned waters and efflorescences has been considered essential for a proper planification of the restoration plan to be applied in the near future in the zone.

1. Introduction

In the vicinity of Huelva (south-western coast of Spain), a large industrial complex is located since the 60's, which included several plants devoted to the production of phosphoric acid [Bolívar et al. 1996a]. The phosphoric acid production process in these plants was based on the acid digestion and dissolution of the feedstock (phosphate rock (PR) mainly coming from Morocco [Bolívar et al. 1996a]) with sulphuric acid, generating a waste called phosphogypsum (PG). Over the past 40 years some 120 million tonnes of phosphogypsum has been generated by the Huelva phosphoric acid plants.

The Moroccan PR treated in the plants is characterized for containing a high concentration of ²³⁸U (around 1500 Bqkg⁻¹, [Betti et al. 2004]) with all its daughter products in secular equilibrium. In the production process about 100% of ²²⁶Ra, 90% of ²¹⁰Pb and 10-30% of the uranium isotopes, originally present in the PR, ends associated to the PG [Bolívar et al. 1996b]. The PG, as a consequence, should be considered as a NORM compound.

Due to the lack of market, historically the great majority of the generated PG has been considered as a residue, with the following management policy applied: a) During the first 30 years of production, 20% of the PG generated was released directly to the Huelva estuary while the remaining 80% was transported from the production plants in suspension with sea water to a neighbouring marshland area where it was disposed by decantation while the transporting waters were draining to the estuary [Periañez et al., 2005], b) since 1998, the direct release of PG to the estuary was banned, hence near 100%

of the PG transported to the neighbouring marshland area to be piled in height. The PG was transported to the disposal area with fresh water, but now the waters follow a closed cycle in order to avoid any impact on the estuarine ecosystem [Más et al.2005].

Since 31st December 2010 the production plants of phosphoric acid were closed, and the production of PG stopped. A legacy after this closing was a big extension accumulating million tonnes of PG that needs remediation or restoration. Currently there is a plan under study in order to restore these PG piles that should solve one of the main problems associated with the actual status of the PG zone: its environmental impact in the neighbouring areas. There exist both direct and diffuse pollution points due to liquid effluents coming from the PG storage deposit (leachates), generated by rainwater and the tidal influence.

The landfill leachates are also the source of “efflorescences” (crystallized/precipitated salts in the water drainage coming from the phosphogypsum pile). In general, the water-soluble efflorescent salts are formed by the evaporation process of water during dry seasons, which produces a large variety of metal hydrosulphates [Alpers et al. 1994]. These processes usually occur on the banks of rivers, but efflorescences can also be formed by capillary migration of water in the surroundings of the tailings or waste piles (as is the case here). The efflorescent salts sequester acidity, metals and radionuclides temporarily and release them later during rain events [Keith et al. 2001]. This means that knowledge of efflorescent salt composition is necessary for prediction of environmental mobility and related impact.

Taking into account the above evidences, the main objective of this work has been the radioactive characterization of the efflorescences and of leaching waters located on the phosphogypsum storage deposits and their surroundings.

2. Materials and methods

2.1 Study area

The PG disposal area can be considered formed by two different areas called zone A and zone B, respectively (see Figure 1). Zone A was formed during the first 30 years of the plants operation and is in continuous direct interaction with their surroundings because there is no physical barrier for avoiding the leaching to the estuary. Zone B, was formed during the last 12 years of the plants’ operation, adopting several options to minimize the interaction with their surroundings: therefore zone B is surrounded by a perimetral channel which collects the drainage waters coming from the piles, incorporating them to the closed circuit.

Consequently, in the zone A it has been possible to observe liquid leakages (filtrations), mostly with a certain flow, to the Tinto river and the Rincon and Mendaña marshlands (see Figure 1), while in the zone B these leakages are clearly minor in number. In both zones and in the vicinity of the observed leakage points efflorescences with different structures and colour were also observed.



Figure 1.- Map of the PG deposits, showing the location of the collection points

2.2 Sampling and pre-treatment

Water and efflorescences were sampled in November 2009 in both zones A and B of the phosphogypsum piles (Figure 1). After collection, all solid samples were dried at 105 °C until reaching a constant weight before analysis, while the water samples were filtered by using polycarbonate filters of 0.45 µm pore size.

2.3 Radionuclide determination

The radioactive characterization of all the samples was performed by applying two independent techniques: gamma-ray and alpha-particle spectrometry.

For alpha-particle analyses, a validated radiochemical method based on the sequential isolation of U-isotopes, Th-isotopes and ^{210}Po with extraction chromatographic resins (UTEVA) has been applied [Casacuberta et al. 2011]. After isolation, U- and Th- isotopes were electrodeposited onto stainless steel plates, while the polonium was self-deposited onto silver discs. The recovery yields obtained with this radiochemical procedure ranged between 80–90% for both U and Po, while for Th they were in the range of 50–60%. The alpha-particle determinations were carried out through the use of an EG&G Ortec alpha-particle spectrometer system.

For gamma-ray determinations (performed only on the efflorescence samples), homogenized aliquots were introduced into polypropylene cylindrical containers with a diameter of 6.6 cm, up to a height of 5 cm. Gamma measurements were carried out by using a gamma spectrometry system, with a coaxial hyper-pure Ge detector (extended range type, model GX3519 from Canberra industries), which has a 38% relative

efficiency. The detector was connected to a conventional electronic chain, including a multichannel analyser, and was shielded by 15 cm Fe. The complete procedure of calibration of this gamma spectrometry system is described elsewhere [Perez J.P. et al.2002].

3. Results and discussion

3.1 Waters

Information about the activity concentration of ^{210}Po , U- and Th-isotopes and the pH values in the water samples analyzed are compiled in Table 1. For an easier discussion, the results will be divided in three main groups: perimetral channel of zone B, and leakage waters collected in the surroundings of zone A and B, respectively.

Table 1.- Activity concentration (Bq L⁻¹) in water samples

	A (Bq L ⁻¹)	^{238}U (α)	^{234}U (α)	^{210}Po (α)	^{230}Th (α)	^{232}Th (α)	pH
ZONE A	A-1	34±1	33±1	29±1	0.32±0.02	0.018±0.005	1.72
	A-2	41±1	40±1	25±1	0.47±0.03	0.020±0.006	1.83
	A-3	39±2	38±2	32±1	0.024±0.005	0.002±0.001	-
	A-4	67±2	64±2	40±1	0.34±0.03	0.036±0.011	1.72
	A-5.1	86±3	86±3	39±3	0.27±0.02	0.040±0.008	1.27
	A-5.2	58±5	58±6	20±1	0.21±0.03	0.044±0.010	1.77
ZONE B	B-1.1	63±4	63±4	8.6±0.4	0.71±0.11	0.08±0.03	1.59
	B-1.2	92±11	93±11	12.6±0.6	0.08±0.01	0.010±0.003	1.56
	B-2.1	92±6	88±6	2.5±0.1	0.39±0.08	0.02±0.01	1.7
	B-3	5.8±0.3	5.0±0.2	1.7±0.2	0.06±0.01	0.007±0.003	2.48
	B-4	4.4±0.8	4.1±0.8	23±1	0.09±0.01	0.014±0.005	2.33
	B-6	0.27±0.05	0.26±0.04	3.4±0.2	0.04±0.01	0.008±0.003	1.98
	B-7	225±5	230±5	29±1	1.09±0.08	0.14±0.02	1.41
CHANNEL	PC-1	39±7	38±7	7.5±0.3	1.60±0.20	0.14±0.05	1.83
	PC-2	329±22	331±23	14.6±0.6	23±1	0.30±0.06	1.26
	PC-3	302±13	301±13	12.0±0.5	12±1	0.12±0.04	1.73
	PC-4	235±30	233±30	13.3±0.5	0.70±0.13	0.058±0.010	1.37

Perimeter channel (Samples PC-1 to PC-4): The waters collected from the PC of zone B are characterized by extremely high concentrations of U-isotopes and, although to a lesser extent, high concentrations of ^{210}Po and ^{230}Th . The levels of uranium in these waters are reaching even 300 Bq/L. In addition, these waters present extremely low pH values, (pH < 2). On the other hand, it is interesting to note that when ordering the radionuclides analyzed in the perimeter channel waters by their concentrations, i.e. U-isotopes > ^{210}Po > ^{230}Th , this order is not in agreement with the radionuclide concentration order found in fresh PG samples collected in the zone (^{210}Po > ^{230}Th > U-isotopes). This fact is reflecting simply the different way of binding of these radionuclides to the PG and their solubility in acidic waters: the Uranium is present mostly in some impurities of phosphoric acid that coats the PG grains and were not fully separated in the production process, while the

^{210}Po and ^{230}Th are more strongly adsorbed to the PG grains, resulting in a lower release to and hence concentration in the water.

Surroundings of Zone B: The U concentrations determined in waters percolating from the zone B are also quite high in comparison with the concentrations usually found in uncontaminated sea and surface waters, but at the same time are lower than the concentrations found in the waters from the perimeter channel. There exists a clear correlation between the acidity of the waters analysed and their uranium activity concentrations, with lower concentrations in the samples with relatively higher pH. However, in the leachate waters samples with pH quite similar to the pH in the perimetral channel waters, the uranium activity concentrations are 3 to 5 times lower, which could be explained by considering that waters that leave the piles into the salt marshes could be previously "filtered" by the dam of the piles. In the water samples with higher pH we could not neglect the possibility of some mixture of contaminated waters coming from the pile with waters from the estuary with clearly lower activity concentrations.

The behaviour observed for the uranium isotopes is also broadly observed for ^{230}Th in the percolated waters but a different behaviour is found for ^{210}Po . Being in all the samples analysed the ^{210}Po activity concentrations extremely high in comparison with the found ones in uncontaminated waters, in some cases these activity concentrations are similar or even higher than the found ones in the perimetral channel waters.

Surroundings of zone A: The percolated waters from the zone A are also characterized by high concentrations of the radionuclides from the U-series but the relative abundance of these radionuclides is different than in the waters leaching from zone B. To understand this difference it is necessary to consider that the PG in the zone A was disposed more than 15 years ago and that the disposal area is not separated from the neighboring salt-marshes by any barrier or perimetral channels. The waters draining from the piles go directly to the nearby environment. Consequently, this zone has "lost" with time a fraction of the radionuclides originally present in them, being this fraction higher for the radionuclides less bounded to the PG structure. i.e, more easily dissolved.

This fact explains the results obtained in the analyzed percolation waters for the U-isotopes. The U concentrations found in these waters are high and relatively uniform but at the same time are one order of magnitude lower than the concentrations determined in the perimetral channel, and lower than the higher values found in waters percolating to the surroundings of zone B. On the other hand, the results obtained for the radionuclides initially more strongly bound to the PG structure like ^{230}Th and ^{210}Po do not follow at all the same trend. In spite of the fact of the historical washing of the PG disposed in zone A, the ^{210}Po activity concentrations found nowadays in the waters leaking from zone A are higher even than the collected ones in the perimetral channel.

Radioactive impact of the waters leached from Zone A and B: An evident conclusion after the radiometric analysis is clear: the waters percolating to the estuary from zones A and B are clearly enriched in radionuclides from the uranium series, resulting in a potential radioactive impact in their surroundings. Hydrological studies performed in the area estimate the average annual flow of waters leaching from both areas at $8 \cdot 10^4 \text{ m}^3/\text{year}$. This flow is negligible compared to the flow of the Tinto river which is on average during the last years $90 \cdot 10^6 \text{ m}^3/\text{year}$. Taken into account the differences in flow rates, the impact

on the estuary as a whole is low, but it cannot be neglected in the saltmarshes areas surrounding the stacks.

3.2 Efflorescences

In table 2 are compiled the activity concentrations of ^{238}U , ^{234}U , ^{210}Po , ^{234}Th , ^{226}Ra and ^{210}Pb in the efflorescences collected either in zones A and B, or in the perimetral channel.

In the samples from the perimetral channel the activity concentrations show quite moderate values, even lower than the concentrations of different radionuclides measured in PG samples. On the contrary in the samples from Zone A and B, although the range of activity concentrations is very ample, it is possible to find aliquots containing activity concentrations for the different radionuclides of the uranium series analyzed, one or even two orders of magnitude higher than in the perimetral channel..

The extremely high differences found in the radionuclide levels between efflorescences collected in the perimetral channel and in the zones A and B, is related with their formation process. While the efflorescences collected in the perimetral channel are formed by saturation of some salts at extremely low pH values that induce the majority of radionuclides to remain dissolved, the efflorescences collected in zones A and B are formed by the evaporation of the water from the piles that induce under conditions of near dryness precipitation of metals and radionuclides associated.

In the formation of efflorescences collected from zones A and B, ^{210}Pb is the main radionuclide sequestered, with concentrations generally higher than 1000 Bq kg^{-1} . The activity concentrations of ^{210}Pb are higher than the ^{238}U and ^{226}Ra concentrations in most samples since the precipitation trend of Pb is different to Ra and U [Bolivar et al. 1996a] during the formation of efflorescences.

In relation to ^{226}Ra , it is interesting to remark that the activity concentrations in the efflorescences collected in zone B are generally considerably lower than those found in Zone A, with values lower than 300 Bq kg^{-1} . All this facts allow us to indicate that the presence of the perimetral channel in zone B diminished the activity concentrations of ^{226}Ra in the efflorescences formed in this area.

Special comments deserve the results obtained for the uranium isotopes (as expected we found secular equilibrium between ^{238}U , ^{234}U and ^{234}Th). The range of activity concentrations found for uranium cover a very ample range, although in the majority of samples, the levels of uranium are not the highest among all the radionuclides analyzed, in opposition to the concentrations observed in the leakage waters. This indicates that there is no general preferential tendency of the uranium to be sequestered in the efflorescence structures during their formation.

The detailed radiometric analysis performed in the set of efflorescences analyzed allow us finally to indicate that they can act as a delayed source of radionuclides, either to the nearby aquatic environment, if they dissolve in the waters that sporadically can cover them, or to the atmosphere if some efflorescence dry material is resuspended by the breezes affecting periodically the estuarine area. Consequently, in the restoration plan of the PG piles under study it is essential to include some steps for the removal of the existing

efflorescences as well as for avoiding its future hypothetical formation by banning the possibility that waters from the piles percolates in the surroundings salt-marshes.

Table 2.- Activity concentration (Bq kg⁻¹) in efflorescence samples

	A (Bq/kg)	²³⁸ U (α)	²³⁴ U (α)	²³⁴ Th (γ)	²¹⁰ Pb (γ)	²¹⁰ Po (α)	²²⁶ Ra (γ)	pH
	A-0.1	83±5	79±5	93±8	1491±65	1092±97	1167±27	3
	A-0.2	481±15	497±15	498±40	1996±93	1727±70	1610±36	-
	A-0.3	903±23	910±24	967±45	1061±56	771±75	592±14	-
	A-0.4	4868±357	5151±376	6014±301	820±141	834±33	287±11	1.8
	A-0.5	6562±465	6588±467	7084±349	990±69	698±28	282±13	1.7
	A-1.1	291±11	303±12	313±22	8691±345	3270±870	52±4	2.7
	A-1.2	222±9	235±9	190±5	4177±168	1770±310	111±3	2.8
ZONE A	A-2.1	1041±15	1047±15	1041±43	9235±336	7196±823	49±3	2.8
	A-2.2	221±5	219±5	243±38	2380±107	2123±86	567±16	2.8
	A-2.3	227±15	231±15	271±26	1464±68	1244±178	871±20	5.1
	A-2.4	2176±145	2138±143	1451±113	1516±132	2350±153	666±19	3.1
	A-2.5	1559±48	1583±50	1791±103	71133±2897	28986±3345	278±13	2.4
	A-3	329±11	319±8	330±51	13888±572	3471±559	302±9	2.6
	A-4.1	950±91	925±89	1010±97	562±88	513±19	290±11	2.8
	A-4.2	376±12	384±12	450±48	1042±56	663±45	2186±50	2.4
	A-4.3	8784±847	8540±796	10153±338	2188±104	1003±139	169±8	2.7
	A-4.4	3024±606	3160±631	3033±159	12187±529	4422±720	138±13	3.2
	A-5	358±7	362±7	349±24	1270±62	884±33	62±4	2.5
	B-2.1	787±12	796±12	832±36	1524±66	1160±34	96±3	2.8
	B-2.2	145±6	147±6	137±15	539±32	407±19	25±1	2.3
	B-3	314±7	313±7	169±16	919±45	697±21	27±3	2.5
ZONE B	B-5	1105±17	1088±16	1076±19	10769±420	11312±1722	145±4	2.7
	B-6	7319±696	7225±688	7038±352	4191±304	2906±391	305±14	3.6
	B-7.1	845±45	781±43	840±42	1301±64	1088±83	76±3	2.9
	B-7.2	1658±62	1623±60	1552±33	8472±463	5520±715	172±9	2.4
	PC-1	76±4	71±4	89±8	374±18	303±14	209±5	2.2
	PC-2	13±2	17±2	14±1	105±9	96±5	90±2	2.6

4. Conclusions

In order to gain essential information for the restoration of a phosphogypsum disposal area containing several million tonnes of this by-product, a detailed radiometric determination in their draining waters and in the efflorescences generated from them has been performed.

The acidic waters discharging from the phosphogypsum piles to the surrounding environment contain high concentrations of radionuclides from the uranium series particularly of the U-isotopes, while the activity concentrations for the same radionuclides in the efflorescences, cover an ample range, with the activity concentrations of ²¹⁰Pb and

^{210}Po being very high and, in general, higher than other typical radionuclides of phosphogypsum as ^{226}Ra and ^{238}U . These facts clearly highlight the different trend of the radionuclides from the uranium series in the different processes occurring in the area and affecting their behaviour: dissolution in the acidic waters, incorporation to the efflorescences during their formation, etc.

However, in spite of the general high activity concentrations determined in both draining waters and efflorescences, the relatively low volume of the outflows from the piles in comparison with the water flow in the estuary and the low density of existing efflorescences imply a moderate radioactive environmental impact of the disposal area on the estuary as a whole, although this impact is more important in their surrounding salt-marshes.

5. References

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