NATURAL OCCURRING RADIONUCLIDE WASTE IN SPAIN: THE HUELVA PHOSPHOGYPSUM STACKS CASE

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Abstract

In this paper, the historical evolution in the management of the wastes generated by one paradigmatic NORM industry devoted to the production of phosphoric acid by the so-called wet-acid method is detailed, demonstrating through experimental results the advances performed along the time in order to minimize their ecological and radiological impact. In addition, and also through experimental studies, it is demonstrated that although the controlled disposal of the mentioned residues is an acceptable management option, is not the optimal one, it is possible to find better alternatives, with an extremely limited radiological impact, as substitute of natural gypsum in cement manufacturing, amended of saline soils, improver of the physical properties of soils, or cover material that speeds the degradation of waste materials and extends the useful life of landfills.
The main conclusions obtained from this particular study can be extrapolated to the majority of NORM industries. The recycling of at least a fraction of the NORM residues generated could lead to the production of some co-products with demanding markets, and very limited radiological impact, alternative that should be encouraged.

Keywords: phosphogypsum, radioactivity, NORM waste, valorization.

INTRODUCTION

Since more than twenty years ago, is increasing the conscience about the necessity to evaluate the environmental and occupational radiological impact generated by the so called NORM industries. These types of industries are characterized either for using raw materials enriched in natural radionuclides or for generating by-products or residues also enriched in these radionuclides, and should be evaluated in order to define if it is necessary to apply some type of regulation to maintain the possible increments in the occupational and public doses caused by them in acceptable levels.

The radioactive and radiological impact of the by-products/wastes generated by this type of industries is in general very much dependent of the management options adopted with them. Historically, the management of these NORM residues has been devotes to minimize its radiological impact. Indeed, especially during the last decade, it is increasing the opinion of the best management option, i.e., to find some marketable applications for the so-called NORM residues, and can be considered them like valuable resources. Obviously, the radiological, environmental and health impact of these co-products in their possible applications should fulfill the limitations imposed by the existing regulations at national and/or international level.

Since 1968, in the vicinity of the town of Huelva (Southwest of Spain), and just in the estuary conformed by the confluence of the Odiel and Tinto River mouths, it is located a big chemical complex, which includes five plants devoted to producing of phosphoric acid by the so-called "wet acid method". This factory generates huge amounts of a by-product called phosphogypsum (PG) which needs an appropriate management because contains enriched amounts of several natural radionuclides, and particularly ^{226}Ra.

In this paper, a detailed description of the main changes performed along the time in the management of the PG produced in the Spanish factory is included, together with examples about the possible applications of this residue, a description of the production process used in the phosphoric acid plant, and a radioactive characterization of the PG it is included.

The history phosphogypsum at Huelva

The Huelva phosphoric acid plants start their activities just forty years ago. Nowadays they are the biggest producers of phosphoric acid in the European Union. Annually are treated about $2{\cdot}10^6$ t of phosphate rock (PR), mostly of the Moroccan origin, being produced about $2{\cdot}10^6$ t phosphoric acid (PA, with 27% P_2O_5) and $3{\cdot}10^6$ t of PG.

During the first 30 years of functioning (until 1998) the management of PG was as follows: a) 20% of the PG were directly released into the Odiel estuary, just in front of the factories (Figure 1); b) the remaining 80% were stored in piles, with about 5-6 m in height and covering over 1200 ha, and the transportation of PG was by pumping it in seawater that, after of the PG decantation, was released into the Tinto river at a pH around 1.5 and with high pollutants concentrations.

The management policy applied during the first 30 years produced a clear radioactive impact in the surrounding environments. Waters and sediments of the Odiel River, and the salt-marshes and vegetation located in their surroundings, were clearly affected by the direct PG releases from the radioactive point of view [1-2].

Since 1998, the waste management policy of the generated phosphogypsum changed drastically. The disposal technique was clearly improved since 1998 due to the formation of a big pyramidal stack covering an extension of 150 hectares, and a height of 30 meters (Figure 1). The PG is transported into this stack from the factory suspended in fresh water where it decants, following these waters a close circuit, i.e., the waters return to the factory to be used both in the production process and to transport newly the PG, avoiding in this way its interaction with the environment. In addition, the new stack is surrounded by a perimetral channel that collects the stack leachates, which are incorporated into the close circuit.

The new PG management policy has produced a drastic reduction of its environmental radioactive impact, allowing the natural radioactive restoration of the previously contaminated estuary, as it has been reflected in several works [3], and concluding that direct public radiological impact of the new stack can be considered practically null. On the other hand, both ^{222}Rn exhalation and re-suspended particulate material do not produce the observation of detectable increments in radionuclide concentrations in their surroundings [4].

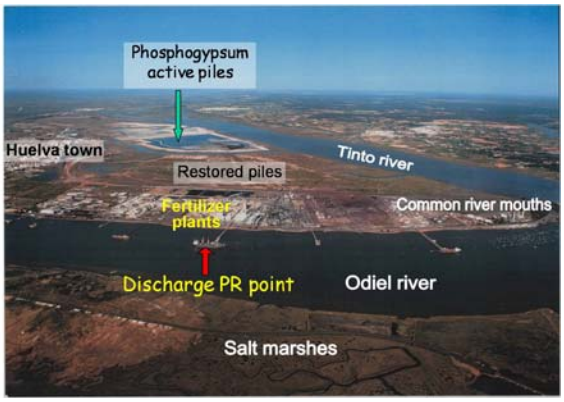

Figure 1. Photography of the zone where are located the Phosphogypsum stacks of Huelva.

Finally, it is also very interesting to mention that a big fraction of the area formerly used by the disposal of the PG (from 1968 until 1997) has been in the last years restored, by covering it with a layer of at least 40 cm of soil. This PG coverage reduces the external gamma dose rates to practically background values, and reduces enormously the amount of ^{222}Rn exhaling [5]. In addition, these restored areas have been re-vegetated trying to adapt them as much as possible to the surrounding unaffected environment.

RESULTS AND DISCUSSION

Previous studies have demonstrated that raw material (Phosphate Rock, PR) used in the production of phosphoric acid contains about 1500 Bq/kg of ^{238}U and daughters (50 times higher than normal soils), and more than 95% of Ra and Po, 70% Th and 25% U initially in PR remain in the PG [6], being ^{226}Ra and ^{230}Th the most radiological dangerous radionuclides. On the contrary, the levels in PG of Th-series radionuclides are smaller than unperturbed soils (see table 1).

The disposal way of PG in Huelva changed at the end of 1997 year, and could be considered as an adecuate option from the environmental and radiological point of view. However, There is the need to find applications of PG in different marketable products. In other words, the total or partial recycling of the phosphogypsum should be considered as the optimal way to deal it with this by-product.

Table 1. Average radionuclide concentrations (Bq kg^{-1}) in PG of Huelva (N = 50 samples). Average activity concentrations in Spanish soils for both ^{238}U and ^{232}Th series radionuclides are around 30-40 Bq kg^{-1}

Isotope	^{226}Ra	^{228}Ra	^{137}Cs	^{40}K
Average	670 ± 50	9 ± 2	< 0.8	15 ± 10
Isotope	^{210}Pb	^{238}U	^{232}Th	^{230}Th
Average	520 ± 60	220 ± 90	8 ± 3	450 ± 60

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The first use of PG of Huelva it has been from 1972 as amendment for the reclamation of soils from the salt-marsh area of the Guadalquivir River (90 km far away from the phosphoric acid plants), application accepted by the Royal Decree 824/2005, from July 2005. The radiological impact associated to the use of the PG in its application in agriculture even at high doses rates (25 ton per hectare) has been demonstrated that generates a negligible radiological impact [7]. We can then affirm highlighting that all the experimental evidence indicates that current practice of PG amendment could still continue safely for several decades in compliance with current radiological regulations.

Glass and glass-ceramics through vitrification processes can be readily manufactured from PG and tailings sand. These products inhibit the emanation of radon from the product, thus eliminating this potential health risk. Products range from glass—ceramic floor, wall and roof tile; and container glass for selected beverages and agricultural products, and it has been demonstrated that radiological impact on the public and workers is one order of magnitude below the legal limits [8].

PG can be also used as a binder for base course mixtures. The stability of compacted PG mixtures is superior to that of clay mixtures. In studies of experimental roads it was concluded that gamma levels from the roadbeds do not yield doses that approach the limit of 1 mSv for a member of the public, and there are no significant effects of radon levels from the roads. Furthermore, investigation of groundwater and soil has shown no significant increase in ^{226}Ra levels due to the presence of the roadbeds [9]

Bench and pilot scale testing indicates that PG used as a cover material speeds the degradation of waste materials and extends the useful life of landfills. There is good evidence to suggest that the addition of PG could enhance biodegradation of municipal solid waste (MSW) in the landfill. During the early stages of waste decomposition in a landfill, the degradation process is essentially aerobic, i.e. with available oxygen, and being carbon dioxide the principal gas produced (complex organics + $O_2 \rightarrow CO_2 + H_2O + SO_4^{2-}$). As oxygen in the landfill is depleted the decomposition process becomes anaerobic, and other gases, principally methane, are generated (complex organics $\rightarrow CO_2 + CH_4 + H_2S + NH_4^+$). Since the PG is enriched with sulfate, it is reasonable to assume that a sulfate using bacterial colony present in landfills could use PG as an energy source after oxygen is depleted. It is therefore anticipated that the use of PG as landfill cover will enhance biological decomposition of MSW and at the same time reduce the accumulation of PG and the volume of cover material remaining in a MSW landfill [10]

CONCLUSIONS

The historical evolution in the management of huge amounts of PG generated the NORM industry devoted to the production of phosphoric acid by the wet-acid method has been reviewed and evaluated critically. This management policy has improved over the time, decreasing to negligible levels the both public and environmental radiological impact of the generated residues.

Associated to the mentioned management, there is nowadays a clear tendency to increase the progressive valorization of the wastes generated by NORM industries in different markets, if the radiological, environmental and health impacts of their applications fulfill the existing regulations. In this paper, several valorization examples have been reviewed in order to show the safe use of the PG in these commercial applications.

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