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External radiation assessment in a wet phosphoric acid production plant

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ABSTRACT

The factories dedicated to the production of phosphoric acid by the so-called wet acid method are usually considered typical NORM industries, because the phosphate rock used as raw material usually contains high concentrations of ^{238}U-series radionuclides. The magnitude and behaviour of the radionuclides involved in the production process revealed the need to determine its dosimetric impact on workers. This work aims to partially compensate this lack of knowledge through the determination of external effective dose rates at different zones in the process at a typical plant located in the southwest of Spain. To this end, two dosimetric sampling campaigns have been carried out at this phosphoric acid production plant. The first sampling was carried out when phosphate rocks originating in Morocco were processed, and the second one when phosphate rock processed came from the Kola Peninsula (Russia Federation). This differentiation was necessary because the activity concentrations are almost one order of magnitude higher in Moroccan phosphate rock than in Kola phosphate rock.

The results obtained have reflected external dose rate enhancements as high as 1.4 μSv h^{-1} (i.e., up to thirty times the external exposition due to radionuclides in unperturbed soils) at several points in the facility, particularly where the digested rock (pulp) is filtered. However, the most problematic points are characterised by a small occupation factor. That means that the increment in the annual effective external gamma dose received by the most-exposed worker is clearly below 1 mSv (European Commission limit for the general population) under normal production. Nevertheless, special care in the design and schedule of cleaning and maintaining work in the areas with high doses should be taken in order to avoid any possibility of exceeding the previously mentioned general population limit.

In addition, the results of the dosimetric campaign showed no clear correlation between ^{226,228}Ra activity concentrations in the material fluxing during the process (the most important radionuclides from the dosimetric point of view) and the external dose rates. Furthermore, any general dependence of the origin of the rock (i.e., on their radioactive contents) on the external effective dose rate measured has not been observed. These latter findings could be a consequence of three effects: (1) a variable radiation shielding at the different points along the process, (2) a changing geometry of irradiation (from a rock pile up to a thin-layered pulp passing through a solid mass inside pipes and deposits), and (3) the existence of a "memory effect", or background contamination in the installation equipment due to the presence of radionuclide-enriched scales and sludges in pipes and deposits.

1. Introduction

Phosphoric acid production plants by the wet acid method are among the best-known NORM-industries (IAEA, 2007). The Royal Decree 783/2001 transposed the European Directive 96/29/EC into the Spanish regulatory system. This type of industries needs to be studied in order to determine possible, significant increments in the exposure of workers and the general public, which could not be considered negligible from the radiological protection point of view. After the evaluation of the results obtained, the Spanish regulatory body (the Spanish Nuclear Security Council) should define if the industrial activity analysed is to be regulated and if any correcting measures to decrease the exposure are to be adopted.

A big chemical industrial complex has been located in the vicinity of Huelva city (southwestern Spain), right on the bank of the Huelva estuary, for 40 years. This complex includes several twin plants dedicated to the production of phosphoric acid by treating imported phosphate rock. Nowadays, these plants are the major producers of phosphoric acid in the European Union by the wet method, annually processing more than two million metric tons of phosphate rock (PR).

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Historically, and from the radiological and radioecological point of view, past attention on these twin plants was focused on the assessment of their radioactive environmental impact caused by the releases and disposal of their residues (Martinez Aguirre et al., 1994; Bolívar et al., 1995, 2000; Periáñez, 2005; Aguado et al., 2004). However, there was until now a certain lack of knowledge of the behaviour and fractionation of radionuclides during the production process, the location of radionuclide sinks (if any) inside the plants and, especially, of the radiological effect of these industrial practises on workers, as estimated from radiation exposure. This is of special concern in order to keep the workers' occupational risk to a minimum, as they are exposed to different materials with high U-series radionuclides in their daily work.

The Huelva plants mainly process Moroccan sedimentary phosphate rock containing ^{238}U-series radionuclides at activity concentrations in the order of 1300–1500 Bq kg^{-1}. However, they also sporadically treat phosphate rocks from the Kola Peninsula, with the ^{238}U-series activity concentration dropping to 75 Bq kg^{-1}, and with activity concentrations of 100 Bq kg^{-1} for ^{232}Th-series isotopes (Pérez, 2005). The main difference among both types of rocks is based in their respective origins: Morocco ore is a sedimentary rock (phosphorite, $Ca_3(PO_4)_2$), while Kola ore is an igneous rock ($3Ca_3(PO_4)_2CaF_2$) having higher P_2O_5 and F_2O_3 contents than Morocco ore. On the contrary, phosphorite shows a higher contents of SO_3 (Pérez, 2005). The differences in geological origins lead to very different rhythms for radionuclide accumulation and, as a consequence, very different radionuclide contents.

This work is the continuation of a previously published paper dealing with the behaviour of natural radionuclides through this industrial process (Bolívar et al., 2009). That work was focused on the fractionation of radioactive equilibrium appearing when the phosphate rock having Moroccan origin is processed. On the contrary, this work reflects the external dosimetric impact of this process on workers. Furthermore, it has been performed a complete comparison of results obtained when both materials (Morocco and Kola phosphate rocks) are processed in the factory.

The radioactive content determined in some key representative samples (raw material, intermediate material, waters, wastes, etc.) has been included in this paper. Those samples were collected when both rock types were being processed in order to analyse the possible correlations between the external exposures measured at different points of the plants and the radionuclide amounts fluxing through them. The element fractionation produced during the industrial process should produce, at least theoretically, quantitative variations of external doses at different points within the factory.

According to the working practices inside the phosphoric acid production plants, two main routes of occupational radiation exposure should be considered: (a) external irradiation, and (b) inhalation. The studies dedicated to inhalation are now in progress, thus this work is dedicated to the evaluation of the external irradiation route. Consequently, the main aims of this work have been: (1) to establish the external dose rates received by workers at several points during the industrial process, (2) the identification, if it exists, of possible "hot points" where the received doses could be so high as to require regulation, and (3) testing if the processing of different-origin rocks (i.e., Morocco vs. Kola) produces important differences in such doses.

A brief description of the process of phosphoric acid production in the plant analysed is required for a better understanding of the radiometric and dosimetric results, and this appears in the following paragraphs. Afterwards the radionuclide results determined in the collected samples (both for Kola and Morocco rock) are briefly discussed. This is a prior, essential step in order to evaluate the magnitude of the different radionuclides entering the process. Furthermore, it allows to analyse the possible correlations between the instantaneous external gamma dose rates measured at different points of the plants and the radionuclide amounts there involved, as it is done in the last section of the paper.

2. Description of the phosphoric acid production process in the plant

The phosphoric production process at the facility is based on the dissolution of the phosphate ore by leaching with sulphuric acid. To summarise, this process consists of four main stages: (1) milling, (2) reaction, (3) filtration/washings, and (4) concentration.

The commercial phosphate rock (on what follows, PR) is initially stored in big silos (Fig. 1), from where it is transported to a ball mill where its grain size is adjusted for an optimum attack during the acid reaction stage. Then, the milled phosphate rock is carried to a separator where only grains with an optimum size (<2 mm in diameter) are selected for the subsequent leaching. The remaining particles are sent to be milled again.

Fine particles feed a reactor of seven compartments (Fig. 2) where they react with 60% H_2SO_4, following the exothermic reaction:

$$Ca_{10}(PO_4)_6F_2CO_3Ca + 11H_2SO_4 + 21H_2O \rightarrow 6H_3PO_4 + 11CaSO_4 \cdot 2H_2O + 2FH + CO_2 \quad (1)$$

This reaction produces a pulp containing a liquid phase (the so-called production phosphoric acid with a P_2O_5 content of 27%) and a solid phase (phosphogypsum, $CaSO_4 \cdot 2H_2O$) as a waste. According to the previous study (Bolívar et al., 2009), which is based on the use of Moroccan phosphate rock, a clear fractionation of radioactive isotopes is produced during this stage. This way, the highest proportion of Ra and Po isotopes remains accumulated in the phosphogypsum (PG), while the tendency to follow the phosphoric acid fraction can be summarised as: U-isotopes $\gg$ ^{230}Th $\geq$ ^{210}Pb $>$ ^{226}Ra. To improve the reaction recovery of phosphorus, a high fraction of the pulp involved in the reaction is forced to circulate in the reactor between the compartments.

The PG is then separated from the phosphoric acid by filtration (Fig. 3). Afterwards it undergoes four successive washings (also Fig. 3) to recover the maximum amount of P_2O_5, and then is pumped into the disposal piles, while the acid fraction is sent to the concentration stage. In fact, the separated acid (called production acid, 27% P_2O_5) is firstly pumped to a decantation

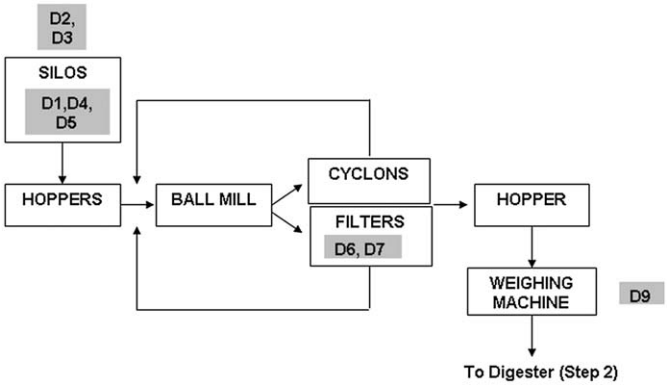

Fig. 1. Schematic diagram of the phosphate rock milling step showing the approximate locations for dose rate measurements.