

# 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 <sup>238</sup>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  $1.4 \mu\text{Sv h}^{-1}$  (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 <sup>226,228</sup>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 (Martínez Aguirre et al., 1994; Bolívar et al., 1995, 2000; Perriñez, 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  $^{238}\text{U}$ -series radionuclides at activity concentrations in the order of 1300–1500 Bq kg<sup>-1</sup>. However, they also sporadically treat phosphate rocks from the Kola Peninsula, with the  $^{238}\text{U}$ -series activity concentration dropping to 75 Bq kg<sup>-1</sup>, and with activity concentrations of 100 Bq kg<sup>-1</sup> for  $^{232}\text{Th}$ -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,  $\text{Ca}_3(\text{PO}_4)_2$ ), while Kola ore is an igneous rock ( $3\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$ ) having higher  $\text{P}_2\text{O}_5$  and  $\text{F}_2\text{O}_3$  contents than Morocco ore. On the contrary, phosphorite shows a higher content of  $\text{SO}_3$  (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

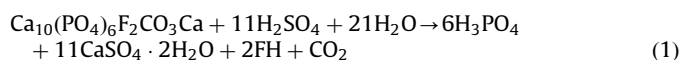
process. Furthermore, it allows to analyse the possible correlations between the instantaneous external gamma dose rates measured at different points of the plants and the radionuclide amounts there involved, as it is done in the last section of the paper.

## 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%  $\text{H}_2\text{SO}_4$ , following the exothermic reaction:



This reaction produces a pulp containing a liquid phase (the so-called production phosphoric acid with a  $\text{P}_2\text{O}_5$  content of 27%) and a solid phase (phosphogypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) 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  $\geq ^{230}\text{Th} \geq ^{210}\text{Pb} > ^{226}\text{Ra}$ . 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  $\text{P}_2\text{O}_5$ , 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%  $\text{P}_2\text{O}_5$ ) is firstly pumped to a decantation

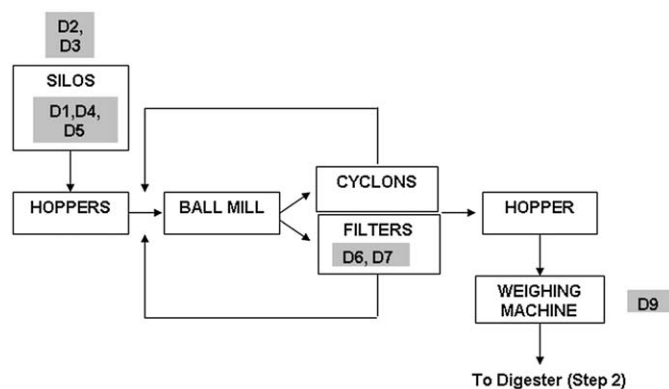


Fig. 1. Schematic diagram of the phosphate rock milling step showing the approximate locations for dose rate measurements.



submitted to calibration checking. Energy dependence of dosimeter response is around  $\pm 30\%$  within the working energy range.

The data reading obtained with this equipment was corrected by contributions arising from cosmic radiation ( $\sim 45 \text{ nSv h}^{-1}$ ) (UNSCEAR, 2000), and electronic noise ( $\sim 40 \text{ nSv h}^{-1}$ ). This latter one was determined through three replicate measurements of background inside the Fe shielding of the Ge gamma spectrometer used in this work. The data set shown in this paper are corrected by those contributions and also by the natural gamma radiation arising from radionuclides in non-perturbed soils ( $\sim 39 \text{ nSv h}^{-1}$ ), which was determined outside the facility. Expressing the results in this way, a direct indication of external dose rate increment above the natural background is performed. Each external dose rate increment data shown in this paper is the result of the average of five 1-min replicate readings. The corresponding statistical dispersion (one standard deviation) of the five replicate readings was always within a 10% range.

Two dosimetric campaigns were performed inside one of the twin Huelva plants in order to construct in detail its external exposure maps depending on the ore origin. Each dosimetric campaign corresponds to the processing of phosphate rock of different origin and radionuclide content.

The factory mostly deals with Moroccan phosphate rock, although Kola raw ore is sometimes used for a few weeks. It was expected that relevant differences in the external dose rates could be reached depending on the origin of the phosphate rock being processed within the factory because their radionuclide content differs notably, as will be shown later. To test this hypothesis, relevant samples (from the point of view of mass/activities balances) were selected in order to look for possible correlations of their radionuclide content with the external rate measurements. A complete analysis of the radionuclide fluxes in the plant process has already been done for Morocco rock (Bolívar et al., 2009), with objectives that differ from those in this work.

$^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{210}\text{Po}$  were analysed in the selected samples by alpha particle spectrometry after radiochemical separation (San Miguel et al., 2001) using eight EG&G Ortec ion-implanted silicon detectors. Other radionuclides were analysed by gamma-ray spectrometry using a coaxial hyper-pure Ge detector (Canberra GX319). Details of characteristics and calibration have been already published by San Miguel et al. (2004). The samples to be measured by gamma-spectrometry were stored after sealing (in order to avoid Rn diffusion) by at least six months before any analysis.  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were measured through the gamma emissions from  $^{214}\text{Pb}$  (352 keV) and  $^{228}\text{Ac}$  (911 keV), respectively, while  $^{228}\text{Th}$  was determined using the 583 keV emission from  $^{208}\text{Tl}$ .

## 4. Results and discussion

### 4.1. Radiometric determinations

Table 1 presents the characteristics inside the process of the analysed samples (for location see Figs. 1–3), while Tables 2 and 3 compile the radionuclide results obtained after their analysis when phosphate rock from Morocco and Kola, respectively, were being processed. For location within the facility see Figs. 1–3.

The analysis of this set of results allows us to draw the following conclusions:

(a) The phosphate rock from Morocco is clearly enriched in radionuclides from the uranium series (sample A2, Table 1), being concentrations at least 50 times higher than in representative unperturbed soils worldwide (UNSCEAR, 2000). All the members of the uranium series are in secular

**Table 1**

Description of the most representative samples collected in the industrial process for natural radionuclides quantification.

Code	Description
<b>Acid attack</b>	
A-2	Grinded phosphate rock feeding the digester
A-1	22% $\text{P}_2\text{O}_5$ extracted from the PG in the first washing and used for favouring the reaction in the digesters
A-5	Pulp formed in the digester, and collected from the compartment 5
A-6	Water just before transportation to the filtration stage, returning to the factory from the ponds used for the storage of phosphogypsum
A-9	Water mixture of fresh water supplied from a neighbouring reservoir and recycled water, returning to the factory from the ponds used for the storage of phosphogypsum. Used to dilute the sulphuric 98%
<b>Filtering and washing</b>	
F-2	27% $\text{P}_2\text{O}_5$ extracted from the pulp coming from the digesters by suction
F-5	12% $\text{P}_2\text{O}_5$ extracted from the PG in the second washing and used for the performance of the first washing
F-7	5% phosphoric acid extracted from the PG in the third washing and used for the performance of the second washing
F-3	PG before to be washed, and after the extraction of 27% $\text{P}_2\text{O}_5$
F-6	PG collected after the first washing with 12% $\text{P}_2\text{O}_5$
F-8	PG collected after the second washing with 5% $\text{P}_2\text{O}_5$
F-11	"Fresh PG" collected after third washing, just before mixing with the recycled waters for transportation to the disposal ponds

equilibrium. In this raw material, the activity concentrations of the radionuclides belonging to the thorium series turn out to be quite reduced (50–100 times lower than uranium series activity concentrations). By contrast, radionuclide contents from the U-series in the Kola PR (sample A2-K) are clearly lower than in the Moroccan one. Activity concentrations from the uranium series radionuclides are only slightly higher than in representative unperturbed soils worldwide (a factor 20 lower than in the PR from Morocco), while activity concentrations from the radionuclides belonging to the thorium series, are slightly higher (a factor of 3) than in the PR from Morocco.

(b) In the reaction stage, it is possible to observe clear evidence indicating the different behaviour of the radionuclides involved after the acid attack of the PR, when both rock types are processed. The uranium isotopes tend to be associated to the liquid fractions of the pulp formed in the digester (samples A5L and A5L-K), which correspond mainly to the phosphoric acid (PA) formed at this stage. This association to the liquid fraction is lower for the thorium isotopes and can be considered negligible for the radium isotopes and  $^{210}\text{Pb}$ . On the contrary, the solid fraction of the pulp (samples A5S and A5S-K) contain the majority of the radium isotopes and  $^{210}\text{Pb}$  originally present in the PR, and a significant fraction of the thorium isotopes. This solid fraction is mostly composed of the phosphogypsum (PG) formed in the reaction of the PR with sulphuric acid (SA), but it may also contain a proportion of non-attacked phosphate rock and some phosphoric acid occluded between the PG grains and poorly separated from the liquid samples. The occlusion of some PA in the pulp solid fraction can explain the results obtained in these solid aliquots for the uranium isotopes. But, in order to understand the uranium-isotopes radionuclide balance in this reaction stage, it is also necessary to take into account that there are two different inputs of radionuclides entering the digester. In addition to the main input associated to the phosphate rock, a significant amount of 22%  $\text{P}_2\text{O}_5$  (about two tons per ton of PR) coming from the later washing stage is entering the digester in order to help the reaction (dissolution) of PR, and a certain amount of water for the dilution of the concentrated sulphuric

**Table 2**  
Natural radionuclides activity concentrations (Bq kg<sup>-1</sup>) obtained in the samples collected at the facility when Moroccan phosphate rock was being processed.

Sample code	Sample type	<sup>238</sup> U	<sup>234</sup> U	<sup>230</sup> Th	<sup>226</sup> Ra	<sup>210</sup> Pb	<sup>232</sup> Th	<sup>228</sup> Th	<sup>228</sup> Ra
A2	Rock	1680±100	1680±10	1670±80	1380±70	1440±100	33±4	17±1	20±1
A1	22% P <sub>2</sub> O <sub>5</sub>	870±50	870±50	95±4	3.0±0.4	74±14	53±11	1.7±0.4	<1.8
A5L	Pulp from reactor	1340±90	1330±90	425±78	4.0±0.4	60±12	6.5±1.4	4.0±0.5	<1.0
A5S		450±30	450±30	750±30	590±25	590±120	16±2	11±1	9.4±1.1
A6	Waters	202±14	202±13	<0.1	4.0±0.4	89±17	0.55±0.14	1.5±0.4	<1.6
A9		0.44±0.02	0.45±0.02	0.027±0.011	<0.4	N.M.	0.007±0.001	<0.8	<0.4
F2	27% P <sub>2</sub> O <sub>5</sub>	1070±110	1090±110	230±30	5.6±0.5	78±15	9.8±1.8	3.9±0.5	<1.8
F5	12% P <sub>2</sub> O <sub>5</sub>	470±40	470±40	80±10	6.1±0.5	<225	6.0±1.5	<1.7	<1.9
F7	5% P <sub>2</sub> O <sub>5</sub>	290±20	290±20	4.2±0.3	1.8±0.3	<135	0.17±0.06	<1.0	<1.5
F3	Gypsum 1	650±40	650±40	760±40	580±30	600±120	34±3	9.0±0.9	9.5±1.6
F6	Gypsum 2	370±25	380±25	790±50	640±30	640±120	19±3	14.3±1.1	9.7±1.3
F8	Gypsum 3	360±25	390±25	720±40	650±35	620±60	31±4	7.8±0.6	11.8±1.0
F11	Gypsum 4	318±26	334±27	830±52	670±35	620±60	18±3	<2.2	10.6±1.2

**Table 3**  
Natural radionuclides activity concentrations (Bq kg<sup>-1</sup>) obtained in the samples collected at the facility when phosphate rock from Kola was being processed.

Sample code (Kola)	Sample type	<sup>238</sup> U	<sup>234</sup> U	<sup>230</sup> Th	<sup>226</sup> Ra	<sup>210</sup> Pb	<sup>232</sup> Th	<sup>228</sup> Th	<sup>228</sup> Ra
A2K	Rock	72±5	73±5	89±9	69±4	51±8	112±11	91±5	102±6
A1K	22% P <sub>2</sub> O <sub>5</sub>	159±10	158±10	24±3	<0.62	<100	12.3±1.2	28.1±1.5	1.8±0.3
A5LK	Pulp from reactor	174±12	173±12	38±4	0.95±0.01	12.2±1.3	17.2±2.1	25.4±1.2	2.9±0.5
A5SK		83±7	82±7	67±7	43.8±2.3	56±9	43±5	32.4±1.9	46.5±2.8
A6K	Waters	181±26	175±26	3.23±0.25	<0.91	<121	—	1.6±0.4	<1.39
A9K		1.3±0.08	1.38±0.08	0.51±0.03	<0.5	<89	(8.2±0.2)10 <sup>-2</sup>	<0.9	<1.1
F2K	27% P <sub>2</sub> O <sub>5</sub>	101±13	103±12	29.1±2.8	<1.7	<109	19.0±2.0	8.0±0.6	<1.7
F5K	12% P <sub>2</sub> O <sub>5</sub>	87±6	84±6	7.8±0.7	<0.86	<118	2.8±0.4	2.6±0.4	<1.4
F7K	5% P <sub>2</sub> O <sub>5</sub>	45±3	46±3	2.2±0.3	1.8±0.3	<118	1.15±0.18	5.5±0.5	<1.6
F3K	Gypsum 1	142±9	152±9	118±7	44.2±2.4	50±7	40±4	33.3±1.9	43±3
F6K	Gypsum 2	49±3	46±3	43±3	42.8±2.2	40±8	16.5±1.5	18.4±1.1	38.2±2.2
F8K	Gypsum 3	38±3	37±3	44±4	45.8±2.2	<153	19.5±2.2	21.1±1.3	43±3
F11K	Gypsum 4	—	—	45.0±2.2	39.8±2.2	69±10	17.4±1.3	19.6±1.1	44±3

acid is used. Both the 22% P<sub>2</sub>O<sub>5</sub> (samples A1 and A1-K) and the SA dilution waters (samples A9 and A9-K) contain significant amounts of U-isotopes and clearly lower activity concentrations of the radium isotopes and <sup>210</sup>Pb. The SA dilution waters (samples A9 and A9-K) are formed by a mixture of freshwater containing negligible amounts of radioactivity, and recycled water used previously for the transportation of PG to the disposal ponds, which contain increased amounts of U-isotopes and other radionuclides such as <sup>230</sup>Th and <sup>210</sup>Po (samples A6 and A6-K).

- (c) The amounts of the different radionuclides contained in the pulp from the digestion stage strongly depend on the PR being processed. Clearly, higher activity concentrations for the radionuclides of the uranium series are obtained when Moroccan rock is treated. In the case of the radionuclides belonging to the thorium series, the activity concentrations are quite moderate in both cases, with slightly higher values when Kola PR is processed.
- (d) The association of a fraction of the uranium-isotopes to the P<sub>2</sub>O<sub>5</sub> occluded among the PG grains was confirmed by the analysis of several selected samples collected in the filtration stage. The digested pulp is taken from the digester and transported to the filtration area, where it undergoes different processes: (1) pulp is filtered by suction, separating the production 27% P<sub>2</sub>O<sub>5</sub> (samples F2 and F2-K) from the PG (samples F3 and F3-K) and (2) the filtered gypsum then

undergoes different washings. The first washing is carried out with 12% P<sub>2</sub>O<sub>5</sub> (sample F5) produced in a later stage, where the 22% P<sub>2</sub>O<sub>5</sub> (sample A1) used in the digestion stage is produced. The second washing is done with 5% P<sub>2</sub>O<sub>5</sub> (sample F7) producing the 12% P<sub>2</sub>O<sub>5</sub> used in the first washing. The final washing is performed with hot water, producing the 5% P<sub>2</sub>O<sub>5</sub> used in the second washing. In conclusion, the production phosphoric acid (27% P<sub>2</sub>O<sub>5</sub>) is obtained from the filtration stage, which can either be commercialised or concentrated up to 54% to produce complex fertilisers. A set of more diluted PA amounts are used either to improve the reaction in the digestion or in the washings of the PG, and a final amount of phosphogypsum is prepared to be sent to the PG disposal ponds mixed with recycled water.

- (e) We have also analysed the radionuclide content in aliquots of PG collected just after their filtration (samples F3 and F3-K) and after the first (samples F6 and F6-K), the second (samples F8 and F8-K) and the third (samples F11 and F11-K) washings. The results confirm the different behaviour of the uranium isotopes in the process in relation to the other radionuclides involved. This is evident by observing how the uranium activity concentrations decrease in the PG samples after their successive washings. In each PG washing, the strength of the PA used to this end increases after the washing, indicating the liberation of a fraction of the PA occluded in the PG, and the liberation of some uranium associated to it.



The conclusions obtained from the radiometric determinations must be analysed from the dosimetric point of view. It is well documented that Ra isotopes and their short half-life daughters are responsible for more than 75% of external instantaneous dose rates due to photon emitters from unpolluted soils (Mas et al., 2001). For that reason, we expect to find the higher instantaneous external dose rates in the areas of the plant where the Ra isotopes are present in high proportions (although the external exposures can be modulated by factors indicated below). According to this reasoning, quite low external dose rates could be expected near the deposits used for the storage of the production PA and the PA acids, as well as in the area dedicated to the concentration of the produced PA. This could be expected because, regardless of the PR treated, the amounts of Ra isotopes and daughters associated to these acids are quite low. In contrast, higher instantaneous dose rates could be expected in the filtration area, where the filtration and successive washings of the PG are carried out in an open atmosphere with low shielding, as described later. In addition, it can be theoretically expected that higher instantaneous dose rates exist in the filtration area with Moroccan PR rather than with Kola PR, as suggested by the significant differences in the Ra contents in the PG produced during their processings.

#### 4.2. Instantaneous external exposures

As expected from their location in the plant and their characteristics, the increments in the instantaneous external dose

rates measured in the common rooms are very low, even undetectable in some cases (Table 4). These rooms are isolated from the areas where the PR is processed, their walls acting as an effective shield against the gamma radiation. These findings are extremely important from the occupational point of view, because the workers spend the majority of the working time inside these rooms.

Relatively small increments of the instantaneous external exposure were determined in the milling area when Moroccan phosphate rock was in process. Only relatively higher values were found at or inside the silos used for the storage of the PR ( $0.25\text{--}0.37\ \mu\text{Sv h}^{-1}$ ), due to the presence of large amounts of Moroccan phosphorite containing high activity concentrations of  $^{238}\text{U}$ . It is worthy to note that lower values were also measured inside the weighting room (where the workers spend the majority of the time in the area).

Relatively high instantaneous external exposures over background were determined in some locations of the acid storage facilities and the concentration areas. However, the PA acids shown in the previous radiometric discussion contain negligible amounts of Ra isotopes and daughters (main gamma emitters inside the process). Furthermore, no clear and systematic decrease in the exposure rates was observed when Kola PR was under process. This fact can be explained by the formation and accumulation of some sludges either on the bottom of the deposits or floating on the free surface of the acids associated to the storage area. These sludges are mainly formed by small particles of phosphogypsum and organic material which were not

**Table 4**

External effective dose rate increment values above the background obtained at different places (before acid attacks starts) within the facility.

Zone	Site description	$\Delta H_{\text{eff}}^*$ ( $\mu\text{Sv h}^{-1}$ ), Morocco	$\Delta H_{\text{eff}}^*$ ( $\mu\text{Sv h}^{-1}$ ), Kola
<b>Milling area</b>			
D1	Inside the phosphorite silo	0.236	–
D2	At 1 m from the phosphorite silo	0.024	–
D3	In the entrance of the silo	0.356	–
D4	At 1 m from a milled rock pile (A)	0.024	–
D5	At 1 m from a milled rock pile (B)	0.03	–
D6	On the way from the mill to the concentrated $\text{H}_2\text{SO}_4$ tanks	0.036	–
D7	At 1 m from the milling dust filters (A)	0.076	–
D8	At 1 m from the milling dust filters (B)	0.093	–
D9	Inside the room to control the weight of the rock to be milled	0.024	–
	<b>Average milling area</b>	<b><math>0.100 \pm 0.117</math></b>	
<b>Acid storing facilities</b>			
D10	Over the roofs of the production (27% $\text{P}_2\text{O}_5$ ) and recycling (22% $\text{P}_2\text{O}_5$ ) deposits	0.121	0.167
D11	Above the 22% $\text{P}_2\text{O}_5$ acid deposits	0.024	0.156
D12	At 1 m of the recycling acid pipes	0.224	0.133
D13	Above deposits, close to the pipes transporting production acid from the filtration area	0.487	0.395
D14	Above deposits, close to the pipes transporting production acid to the concentration stage	0.064	0.167
	<b>Average acid storage facilities</b>	<b><math>0.184 \pm 0.185</math></b>	<b><math>0.204 \pm 0.108</math></b>
<b>Milling area</b>			
D15	At 2 m from the acid concentration area	0	–
D16	Above the decanter of the production acid	0.196	–
D17	Above the decanter of the production acid, after addition of flocculant	0.053	–
D18	At 0.5 m over the material collected in the overflowing tray of the decanter	0.304	–
D19	At 0.5 m over the deposit storage the sludges collected in the decanter	0.167	–
	<b>Average concentration area</b>	<b><math>0.144 \pm 0.120</math></b>	–
<b>Common rooms</b>			
D20	At the entrance of the plant	<b>N.D.</b>	<b>N.D.</b>
D21	On the facility rooftops	<b>0.024</b>	–
D22	Inside the chemical laboratory	<b>N.D.</b>	–
D23	Inside the plant control room	<b>0</b>	<b>0.036</b>
D24	Inside the old plant control room	<b>N.D.</b>	–
D25	Inside the mill operator cabin	<b>0.013</b>	<b>0.036</b>
	<b>Average common rooms</b>	<b><math>0.012 \pm 0.012</math></b>	<b>0.036</b>

\*"Morocco" and "Kola" indicate the origin of the phosphate rock being processed when the dosimetric campaign was carried out.

separated in the filtration and washing stages previously performed. They precipitate/accumulate on the deposits when the PA acids are stored. The sludges are also observed in the concentration area, and they are separated there when the production PA is subject to decantation. Several of these sludges from the PA deposits were analysed for Moroccan PR processing (Table 5), and the high  $^{226}\text{Ra}$  activity concentrations are evident.

The presence of these sludges and the formation of scales into the pipes used for the transport of the phosphoric acids can explain the effective dose rates measured in both areas, even when Kola PR was being under process. This fact leads to conclude that the obtained external dosimetric determinations are affected by a kind of “memory effect” due to scales and sludges being formed during the processing of Moroccan PR.

Table 6 presents the effective external dose rate increments measured in the remaining areas of the plant. Minor dosimetric increments were registered in the digestion/reaction area in spite of the high radioactive content in the reacting pulp reacting (especially that due to Moroccan rock). This lack of correlation between effective external dose rate and materials radioactive content is probably due to the fact the reactor itself acts as a shield for the emitted radiation. This shielding effect can be illustrated by comparing the values determined above an open digestion block (compartments 3 and 4) and above a closed digestion block (compartments 4 and 5). The external exposures determined over the open block were more than 10 times higher than those measured over the closed block.

The highest effective external dose rates were measured inside the filtration facility, reaching  $1.1\text{--}1.4\ \mu\text{Sv h}^{-1}$  around the third washing stage. The measurements carried out above the filter itself, being a zone with very low occupation factors, show high

external dose rate. The remaining measures were performed along the perimeter of the filter, and lower values were obtained due to radiation attenuation by the metallic lateral walls of the filtration system. The values obtained over the filter are clearly higher than expected in most cases. It is necessary to take into consideration that the values registered at 1 m over a semi-infinite extension of PG hardly surpass  $0.3\ \mu\text{Sv h}^{-1}$  (Mas et al., 2001). Consequently, an additional source of gamma radiation must be present in the filtering area, being a major contributor to the effective dose rate and, additionally, it should be present regardless of the PR rock treated in the process, as presented in Table 6. Therefore, the existence of a permanent radioactive contamination in some parts of the filtering equipment (scales) can be derived. Table 7 presents some radiometric determinations performed on aliquots of a used filter cloth, along with a scale sample collected from the inner surface of a pipe. Quite high  $^{226}\text{Ra}$  activities were determined, supporting the previous statement.

We can then conclude from the external dose rate measurement campaigns that, with the exception of the milling area where only PR is involved, the values obtained for the external exposures cannot be correlated to the amount of radioactivity

**Table 7**  
Natural radionuclides activity concentrations ( $\text{Bq kg}^{-1}$ ) obtained in some “hot” samples collected at the filtration step (see the text for details).

Sample	$^{210}\text{Pb}$	$^{238}\text{U}$	$^{226}\text{Ra}$	$^{228}\text{Th}$	$^{228}\text{Ra}$	$^{40}\text{K}$
Filter clothings	$2330 \pm 110$	$290 \pm 60$	$3340 \pm 130$	$48 \pm 8$	$70 \pm 8$	$< 20$
Filter hoses	$1030 \pm 70$	$570 \pm 80$	$2110 \pm 90$	$28 \pm 7$	$48 \pm 7$	$< 30$
Pipe scales	$2030 \pm 160$	$980 \pm 40$	$1410 \pm 60$	$17 \pm 2$	$29 \pm 2$	$< 20$

**Table 5**  
Natural radionuclides activity concentrations ( $\text{Bq kg}^{-1}$ ) obtained in sludge samples collected at the phosphoric acid decantation tanks (see the text for details).

Sample characteristics	$^{238}\text{U}$	$^{234}\text{U}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{232}\text{Th}$	$^{228}\text{Th}$	$^{228}\text{Ra}$
Bottom sludge	$1230 \pm 70$	$1230 \pm 70$	$2000 \pm 150$	$4300 \pm 220$	$1900 \pm 90$	$28 \pm 6$	$32 \pm 3$	$65 \pm 6$
Floating sludge	$910 \pm 60$	$900 \pm 55$	$910 \pm 25$	$1310 \pm 70$	$1420 \pm 160$	$13 \pm 1$	$10 \pm 1$	$18 \pm 2$

**Table 6**  
External effective dose rate increment values above the background obtained at different places (from the acid attacks onwards) within the facility.

Zone	Site description	$\Delta H_{\text{eff}}^{\text{Morocco}}$ ( $\mu\text{Sv h}^{-1}$ ), Morocco	$\Delta H_{\text{eff}}^{\text{Kola}}$ ( $\mu\text{Sv h}^{-1}$ ), Kola
<b>Digestion area</b>			
D26	Above open reactor compartments 3 and 4	<b>0.087</b>	<b>0.093</b>
D27	At 2 m from the reactor compartments 4–5	<b>N.D.</b>	<b>N.D.</b>
D28	Above compartments 4 and 5 (A)	<b>0</b>	<b>0.042</b>
D29	Above compartments 4 and 5 (B)	<b>0.007</b>	<b>0.042</b>
	<b>Average digestion area</b>	<b><math>0.031 \pm 0.048</math></b>	<b><math>0.059 \pm 0.029</math></b>
<b>Filtration area</b>			
	<i>Over the filtering system</i>		
D30	At 1 m from the pulp entrance to the filter	<b>0.435</b>	<b>0.413</b>
D31	On the way from pulp entrance to the first washing stage	<b>0.755</b>	<b>0.464</b>
D32	At 1 m from the first washing stage using acid with a 12% $\text{P}_2\text{O}_5$ content	<b>1.035</b>	<b>1.006</b>
D34	On the way from the first to the second washing stage (dry gypsum)	<b>0.715</b>	<b>0.544</b>
D35	At 1 m from the 2nd washing using acid with a 5% $\text{P}_2\text{O}_5$ content	<b>0.972</b>	<b>1.115</b>
D36	On the way from the 2nd to the 3rd washing stages	<b>0.886</b>	<b>0.555</b>
D37	At 1 m from the 3rd washing with water	<b>1.103</b>	<b>0.287</b>
D38	At 0.5 m on the way from the third washing to the place where the dry gypsum is titled	<b>1.354</b>	<b>0.344</b>
	<i>Surrounding the filtering system</i>		
D39	At 0.75 m from the filter, on the way from the pulp entrance to the first washing	<b>0.156</b>	<b>0.104</b>
D40	At 0.75 m from the filter, on the way from the first to the second washing	<b>0.156</b>	<b>0.121</b>
D41	At 0.75 m from the filter, on the way from the second to the third washing	<b>0.104</b>	<b>0.156</b>
D42	On the way from the third washing and the place where the gypsum is titled	<b>0.087</b>	<b>0.133</b>
	<b>Average filtration area</b>	<b><math>0.600 \pm 0.458</math></b>	<b><math>0.410 \pm 0.334</math></b>

“Morocco” and “Kola” indicate the origin of the phosphate rock being processed when the dosimetric campaign was carried out.

fluxing by them. Thus, the major fraction of the external exposure rates measured is produced by a permanent radioactive contamination of the pipes, deposits and filtering systems in the plant.

This permanent source can thus explain (1) the high values obtained in the filtration area, (2) the higher than expected values in the storage acid facilities and in the concentration area, and more importantly, (3) the independence of measured effective dose rate on the origin of phosphate rock being processed. This last finding cannot be explained with regard to the radionuclide content in both raw materials. It is worthy to note that  $^{232}\text{Th}$ -series radionuclide activity concentrations are in Kola PR a factor 3 higher than in Moroccan PR. This proportion cannot compensate (from the dosimetric point of view) the largely reversed proportion regarding  $^{238}\text{U}$ -series radionuclide concentrations (Morocco/Kola~50). Such similarities among the instantaneous external dose rate values are clearly shown in Fig. 4. A reasonable correlation ( $r = 0.94278$ ) between the obtained values in both sampling campaigns was observed, once three outliers were removed, though the slope of the fit was slightly less than one ( $0.86 \pm 0.06$ ).

The fixed source of contamination is enriched in  $^{226}\text{Ra}$  (Tables 5 and 7). It has been observed that  $^{226}\text{Ra}/^{228}\text{Ra}$  activity ratio is about 70. This value is in agreement with that found in the Moroccan rock and in the Moroccan PG (no isotope discrimination occurs during the industrial process). This fact suggests using this isotope ratio as a characteristic fingerprint for Moroccan PR. The effect of that fixed contamination source during the sporadic processing of the Kola PR reflects as follows: the analysed samples of Kola PR are characterised by a  $^{226}\text{Ra}/^{228}\text{Ra}$  activity ratio of 0.7. This amount increases in Kola PG samples up to 1.0. The corresponding activity ratios are significantly different. Thus, the presence of Moroccan  $^{226}\text{Ra}$  in the “Kola PG samples” seems evident.

The order of magnitude of maximum values of the effective gamma external dose rates shown here are similar to those published for other types of NORM industries. High values were previously collected during zirconia processing ( $0.62\text{--}2.70 \mu\text{Sv h}^{-1}$ ), rare earth elements industry ( $\sim 1.80 \mu\text{Sv h}^{-1}$ ), baddeleyite ( $\sim 4 \mu\text{Sv h}^{-1}$ ), and in amang processing ( $0.3 \mu\text{Sv h}^{-1}$ ), as reported by Hipkin et al. (1998) and Ismail et al. (2001). Also, as expected, the values in our plant were more than one order of magnitude less than those reported in some specific locations for the oil and gas industry (up to  $50 \mu\text{Sv h}^{-1}$ ; Hamlat et al., 2001).

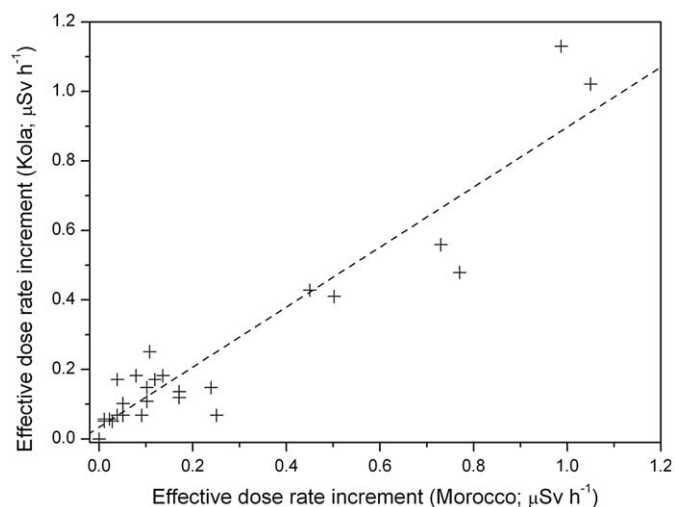


Fig. 4. Linear relationship between the external effective dose rate increments above the background that were sequentially collected when Kola and Morocco phosphate rock were being processed in that facility.

The maximum dosimetric increments inside the phosphoric acid plant are about 20–30 times higher than the equivalent background contribution, a fact to bear in mind when keeping the doses received by workers to a minimum.

Nevertheless, it is important to remark that the area reaching the highest instantaneous external exposures (the filtration facility) is almost completely automated. Thus, the presence of operators in or around the filtration system is almost never required (with the exception of management and repairing tasks). Consequently, these dosimetric “hot points” are also characterised by very low occupational factors. The only exception might be when both maintaining and cleaning tasks are performed, which are necessary as scale deposits prevent matter to flow through the pipes, while the cloth filters need to be changed due to pore saturation. Hence, these tasks require careful scheduling in order to avoid that a high occupation factor could lead to an exposure above the limits described for general population.

Under normal working conditions, the effective external dose rates received by the workers in the plant are quite below  $1 \text{ mSv y}^{-1}$ . A conservative estimation of effective external dose rate received by workers could be done according to the following assumptions:

- (a) an average worker in the plant (2000 working hours per year) spends  $200 \text{ h y}^{-1}$  in each of the following areas (milling area, acid storage facilities, concentration area, digestion area and filtration area),
- (b) the remaining 1000 h are spend working in the common rooms of the plants and
- (c) in each of the areas the instantaneous external dose rates affecting the average worker are taken as the maximum instantaneous value measured in each area (i.e.  $0.251 \mu\text{Sv h}^{-1}$  in the milling area,  $1.369 \mu\text{Sv h}^{-1}$  in the filtration area, Tables 4 and 6).

Under these conditions, the annual effective external dose rate received by the worker will be less than  $0.5 \text{ mSv y}^{-1}$ .

This value should be considered an upper limit being almost impossible to reach for workers in the plant, due to the highly conservative hypothesis adopted for its determination. The workers spend fewer hours than those considered in the areas with higher instantaneous external exposures. Furthermore, in these areas they receive lower instantaneous external exposures than those considered. However, it is necessary to take into consideration that the values shown here only referred to external effective dose rates. As previously explained, some other contributions, especially inhalation, should be monitored, as it represents a non-negligible fraction of the overall effective dose rate received by a worker in the plant (Ismail et al., 2001; Papastefanou, 2001).

## 5. Conclusions

Two external dosimetric monitoring campaigns carried out at a phosphate rock processing plant located at south-western Spain have revealed the existence of several points where the external exposures could reach  $1 \mu\text{Sv h}^{-1}$ . However, the locations where these higher values were obtained are characterised by low occupancy factors on the part of workers in the plant. As consequence, a very conservative estimation reflects that the external effective dose rates received by the workers in the plant never surpasses  $0.5 \text{ mSv y}^{-1}$ .

The dosimetric monitoring campaigns have been carried out when both Morocco and Kola raw ore have been processed. Although their  $^{238}\text{U}$ -series radionuclides content is quite different (the first being almost twenty times higher than the second one),



no systematic differences have been found from the external dose point of view in both campaigns. The relatively high and non-ore dependent instantaneous external doses measured in different areas of the plant should be associated to the existence of a dominant background contamination fixed at different parts of the plant. That is due to the presence of sludges (in deposits) highly enriched in  $^{226}\text{Ra}$ , scales (within pipes) and filters, which greatly contribute to the instantaneous external dose rates measured. In fact, the contamination inside the factory is nonhomogeneous, as locations showing scales have very different geometry and shielding thickness. Under these conditions, it is difficult to show any correlation between the external dose rate performed measurements using a portable equipment and the concentration of samples taken near the measurement points.

The presence of the troublesome points noticed in this work is encouraging for enhancing the study taking into account cumulative external doses (using SSTDs) and internal doses due to Rn and particulate inhalation. That work is currently in progress.

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