

Occupational Exposures and Distribution of Natural Radionuclides in Phosphoric Acid Production by the Wet Process (Spain)

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1. Abstract

The industries devoted to the production of phosphoric acid use as a raw material large amount of phosphate rock (PR), which – depending on its geological origin – could be enriched in natural radionuclides either from the uranium or thorium series. In addition, and depending of the process used, different by-products also enriched in natural radionuclides are formed. For this reason, these types of industries are considered as one of the most representative examples where NORM and TENORM is handled, and consequently where a detailed radiological study for protection of the workers is needed.

In Spain, a quite large industrial complex is located in an estuary in the surroundings of Huelva town (SW of Spain, see Figure 1), with two big factories devoted to the production of phosphoric acid through the so-called “wet-acid process” (see details in Section 2). In these factories, two types of phosphatic ores are processed: a) sedimentary marine origin phosphate ore from Morocco, and b) igneous origin phosphate ore from Kola (Russia).

The Moroccan phosphorites are characterised for their high uranium concentrations, ranging 100-150 ppm, while the igneous phosphate rocks from Kola have clearly lower levels of this element. In opposition, the Kola phosphate rocks present concentrations of the ²³²Th-series in a factor up to 3 to 5 higher than in word average soils, while the Moroccan phosphorites contain clearly lower concentrations from this natural series [1]

In both raw materials, both the ²³⁸U and the ²³²Th are in secular equilibrium with their daughters. Nevertheless, during the application of the industrial process, the aforementioned secular equilibrium is broken, suffering the different radionuclides their redistributions between intermediate products according to their respective chemical characteristics [2]. This fact need to be taken into consideration for a proper radiological study inside the factories.



Figure 1. Picture of the industrial complex located in the Huelva estuary. At the left can be seen partially the town of Huelva, and at the top the phosphogypsum piles can be observed.

For that reason, and after a general description in Section 2 of the different steps of the industrial process applied in the Huelva phosphoric acid industries, Section 3 will be devoted to analyse and follow the radioactivity levels of selected radionuclides throughout the whole industrial process, in order to locate those steps where their radioactivity levels could become enriched or enhanced in relation with the used raw ore.

The information gained with the study described in Section 3, has allowed to design and perform two campaigns in order to determine the external gamma dose rates at different locations of one of the factories, as a first step to determine the occupational exposures of the workers in this type of work place. In the first campaign, the measurements were carried out while phosphate ore from Morocco was under treatment; in opposition, during the second campaign, the mineral processed had its origin in Kola (Russia). The results obtained in both external gamma dose rates campaigns are presented, discussed and compared in Section 4 of this paper.

The “wet acid process” used for the production of phosphoric acid in the factories located in Huelva is characterised by the formation of a by-product called phosphogypsum (a calcium sulphate matrix) [2] that, as it will be shown, contains a considerable fraction of some of the radionuclides originally present in the processed mineral. Huge amounts of this by-product are formed in the Huelva factories (around 2.5 million tonnes per year), which in a big proportion have been accumulated forming big piles in a salt-marsh area located near the factories, less than 0.5 km away from the surroundings of Huelva town. Since the beginning of the operations in the factories (the 1960s) more than 70 million tonnes of phosphogypsum have been accumulated in the aforementioned area, covering an extension of about 1200 Hectares, which constitutes a clear and well known radiological anomaly.

During the last decade, several countermeasures were adopted and applied in this storage area in relation with the management of this by-product and with its transport

from the factories. The objective (covered successfully) was to minimise its radioactive/radiological impact on the close environment and on the public [3, 4]. However, in the maintenance, management and proper formation of the phosphogypsum piles, several workers of the Huelva factories are involved, which radiation exposures need to be controlled. In this sense, Section 5 of this paper will be devoted to expose the main results obtained in: a) the measurement of external gamma-ray dose rates over the piles, and b) the estimation of the doses received by the workers due to inhalation of resuspended particulate material and of radon emanated from the piles.

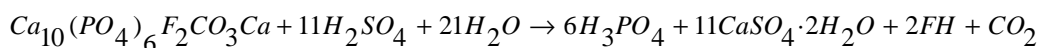
The Spanish administration translated in 2001 year to a national law the whole 96/29 EURATOM directive devoted to the protection of the workers and the public against ionising radiation, including Title VII concerning significant increase in exposure due to natural radiation sources. The work exposed in this paper correspond to one of the pilot studies, still under progress, which under the support of the Spanish Nuclear Security Council (CSN) different research groups are performing in order to obtain contrasted information from several industrial activities in Spain susceptible to be affected by the aforementioned Title VII.

2. Description of the industrial process

The phosphoric acid production process via the “wet acid process” is based on the dissolution of the mineral ore through its leaching with 60% sulphuric acid. The whole process can be divided in four main steps: milling, reaction, filtration and concentration [5].

In the first step, the imported ore is milled using a ball mill, and the milled phosphate is transported by an air stream (generated with a ventilator) to a separator, where only grains with optimum size (0-2 mm particle diameter) are selected. The remaining particles are sent back to the ball mill.

The selected fine particles generated in the first step, are then transported to a cyclone where react with 60% H₂SO₄ (step 2), following the reaction:



Through this reaction, weak phosphoric acid is produced (27% P₂O₅) mixed with phosphogypsum, as a pulp. This reaction need to be carried out at a controlled temperature of 72°C, and for that reason the pulp is re-circulated along different compartments of the reaction chamber.

At this stage, the phosphogypsum should be separated from the phosphoric acid, usually called “production phosphoric acid”. This process is done in the filtration step (step 3), using a PRAYON filter formed by several vacuum-controlled filtering units where, first, most of the phosphoric acid is sucked, and afterwards the phosphogypsum is washed to collect its remaining traces. Each unit (constructed on stainless steel) has a synthetic cloth, resistant to strong acids, placed on its bottom and acting as a filter.

In Table 1, the values obtained for ^{238}U , ^{226}Ra and ^{228}Ra in three samples collected from the milling step are shown. These samples correspond to: a) raw phosphate rock from Morocco, b) milled phosphate rock collected in the ball mill, and c) milled phosphate rock that have passed the separator (optimum grain size for reaction). The obtained results show the elevated concentrations of the radionuclides belonging to the U-series in the treated mineral (1.6-1.8 kBq/kg), and reflect the existence in the three samples of secular equilibrium between the ^{238}U and its daughter, ^{226}Ra . On the other hand, the ^{228}Ra concentrations (radionuclide representative of the Th-series) are similar or even lower than those determined in worldwide representative soils (10-40 Bq/kg).

The elevated concentrations of Uranium and daughters in the phosphate rock, allow clearly its classification as NORM. If in addition, we have in consideration the huge amount of mineral treated in the Huelva factories per year (approx. $1.5 \cdot 10^6$ Tonnes of Moroccan phosphate rock) its is obvious to deduce the importance of the study detailed in this work, on the frame of the aforementioned Title VII of the 96/29 EURATOM directive devoted to the protection of the workers and the public against ionising radiation. A minimum of $2 \cdot 10^{12}$ Bq of ^{238}U (as well as of its daughters) are entering annually, associated to the mineral, in the Huelva factories.

Table 1. Activity concentrations (Bq/kg) determined for radionuclides from Useries (^{238}U , ^{226}Ra) and the thorium series (^{228}Ra) in samples collected from the milling step (step 1) in one of the Huelva factories.

Samples from the milling step. Phosphate rock from Morocco			
Activity concentrations (Bq/kg)			
Sample type	^{238}U	^{226}Ra	^{228}Ra
Raw phosphate rock	1840 ± 130	1560 ± 80	22 ± 2
Buk milled phosphate rock	1640 ± 90	1722 ± 90	20 ± 2
Optimum size phosphate rock	1630 ± 90	1780 ± 90	22 ± 2

In Table 2, the results obtained in the analysis of two samples collected in the reaction step, (step 2), are detailed. These samples were obtained from the reactor where the rock reacts with the sulphuric acid, and correspond to: a) liquid pulp, which is formed essentially by the P_2O_5 resulting from the reaction, and b) solid pulp, which is formed by a mixture of phosphogypsum with small remaining amounts of P_2O_5 , as well as by a determined proportion of phosphate rock not dissolved.

Table 2. Activity concentrations (Bq/kg) determined for radionuclides from Useries (^{238}U , ^{226}Ra) and the thorium series (^{228}Ra) in samples collected from the reaction step (step 2) in one of the Huelva factories.

Samples from the Reaction step. Phosphate rock from Morocco			
Activity concentrations (Bq/kg)			
Sample type	^{238}U	^{226}Ra	^{228}Ra
Liquid pulp	1340 ± 90	5 ± 1	< 1.1
Solid pulp	950 ± 60	811 ± 42	14 ± 2

The results show clearly the existence of radioactive fractionation during the production of the phosphoric acid via the “wet method”. In the reaction step, the uranium, quite soluble, tends to be associated to the phosphoric acid while the radium (as well as the ^{210}Pb and the ^{230}Th) tends to be present in the by-product phosphogypsum. In the solid pulp the concentrations of ^{238}U and ^{226}Ra are quite similar due its special composition (described in the previous paragraph).

In Table 3, are compiled some of the results obtained in the analysis of four samples collected in the filtration step (step 3). These samples correspond to:

- a) phosphogypsum coming from the reactor before its washing (practically this sample can be associated to the solid pulp sample collected in the reaction step),
- b) phosphogypsum after its first washing,
- c) phosphogypsum after second washing, and
- d) phosphogypsum collected after all the programmed washings and collected just before its transport to the storage area.

The results indicate the elevated and stable concentrations of ^{226}Ra in the analysed phosphogypsum samples with independence of the number of washings applied to them, and, at the same time, a systematic decrease in the uranium concentrations when the number of washings increases. This fact demonstrate:

- a) the strong association of the Ra, originally existing in the phosphate rock, to the phosphogypsum fraction (in order to correlate the ^{226}Ra concentrations observed in the phosphogypsum with the originally present in the phosphate rock, it is necessary to take into consideration that for each gram of treated rock approx. 1.5 grams of phosphogypsum is formed), and
- b) the presence of a considerable fraction of ^{238}U detected in the gypsum before its washings, associated with the presence of remaining P_2O_5 . In the successive washings, the fraction of P_2O_5 in the phosphogypsum decreases and, consequently, the amount of uranium.

Table 3. Activity concentrations (Bq/kg) determined for radionuclides from the U-series (^{238}U , ^{226}Ra) and the Th-series (^{228}Ra) in samples collected from the filtration step (step 3) in one of the Huelva factories.

Samples from the filtration step Phosphate rock from Morocco Activity concentrations (Bq/kg)			
Sample type	^{238}U	^{226}Ra	^{228}Ra
Phosphogypsum before washing	810 ± 50	880 ± 40	14 ± 2
Phosphogypsum after first washing	460 ± 30	1040 ± 50	15 ± 2
Phosphogypsum after second washing	450 ± 30	1000 ± 50	17 ± 2
Phosphogypsum to be stored	310 ± 20	900 ± 50	14 ± 2

The strong association of the U to the P₂O₅ was finally confirmed through the analysis of two samples collected in the final step of the process: the concentration step (Table 4). They correspond with two aliquots of P₂O₅ with different degree of concentration. The results indicate the negligible presence of ²²⁶Ra in these samples and the increase in the elevated concentrations of uranium with the increase in the concentration of the acid.

Table 4. Activity concentrations (Bq/kg) determined for radionuclides from the U-series (²³⁸U, ²²⁶Ra) and the thorium series (²²⁸Ra) in samples collected from the concentration step (step 4) in one of the Huelva factories.

Samples from the concentration step Phosphate rock from Morocco Activity concentrations (Bq/kg)			
Sample type	²³⁸ U	²²⁶ Ra	²²⁸ Ra
P ₂ O ₅ 32%	1300 ± 70	4 ± 1	< 1
P ₂ O ₅ 54%	1830 ± 180	8 ± 1	< 1

As it was stated previously, the study that we have shown in this section corresponds only to a minimum but representative fraction of the whole study performed in the factories. In total around 50 samples collected along the industrial process were analysed for the determination of their radioactive content while phosphate rocks from Morocco were being processed. A similar study, by analysing also similar number of samples, was carried out while phosphate rocks from Kola were being treated in the same factory. In both studies, in addition to ²³⁸U, ²²⁶Ra and ²²⁸Ra, the concentrations of other radionuclides like ²³⁰Th, ²¹⁰Pb, ²¹⁰Po, ²³²Th, ²²⁸Th and ⁴⁰K were analysed. The whole set of data has allowed us to perform a complete analysis of the flux of radionuclides along the process when the two types of phosphate rocks were treated. This analysis served us as a basis for a proper design and planification of the radiological studies for protection of the workers inside the factories, and in the area devoted to the storage of the phosphogypsum. In particular, and knowing the radionuclides involved, as well their magnitude at the different places, studies have been performed or are now running in the both aforementioned locations for the determination of the external gamma dose rates susceptible to be received by the workers, as well as for the estimation of the doses received by them through inhalation of particulate matter and radon. Other pathways of radiological impact: digestion, direct dust deposition on the skin, etc, were evaluated as negligible after the study of the industrial process and the labours of the workers.

4. Occupational exposures inside the factories

External absorbed gamma dose rate measurements have been carried out inside the factories using a gas-flow detector Bethold Umo LB123 coupled to a LB1236 probe, which works under proportional regime. All the results obtained were background corrected, including this background the contribution from the detector noise and cosmic radiation according to the data published elsewhere [9], as well as the contribution of background soil. The instrument was properly calibrated, and its performance and calibration is periodically checked. The energy working range of the detector is 30-200 keV.

In Table 5, are shown the increments (above background) of the external absorbed gamma dose rates at different locations inside the facilities and when both types of phosphate rocks (Morocco and Kola) were under process. The most important conclusions, which can be drawn from these results, are the following:

- 1) A quite wide range of increment values have been obtained, existing on the other hand a clear correlation between their magnitude and the zone of the process monitored. The higher increments in the absorbed external gamma dose rates were observed in some locations of the filtration step, while the lower ones were obtained in the more isolated or protected rooms of the facility (laboratory, control room, etc).
- 2) It was not observed systematic differences in the obtained values when the type of phosphate rock under process in the factories was changed. In general, at the same locations, the results were different in the two campaigns in a variable factor, which ranges between 0.5 and 2. The magnitude of these differences could be in principle considered surprising if we take into account that the Kola phosphate rocks contain clearly lower concentrations of the ^{238}U -series radionuclides than the Morocco ones. Nevertheless, it can be explained if we take into consideration the following two arguments: a) the Kola phosphate rocks are enriched, in comparison with the Morocco phosphate rocks, in radionuclides from the ^{232}Th series. Consequently, it is possible the partial compensation of the potential decrease expected in the absorbed gamma dose rate when Kola material is processed due to low concentrations of the U-series radionuclides with an increase due to the higher contribution of the Th.-series radionuclides, and b) The Morocco phosphate ore is the basic and predominant raw material treated in the factory. The use of Kola Material is quite minority. Hence, inside the facilities, reservoirs, deposits, pipes and other parts of the installation could be affected, just before the processing of Kola, for a kind of "memory effect" due to presence in them of an important amount of radionuclides with origin in Moroccan material previously treated. In other words, the dosimetric determinations carried out when the Kola material was under process can be affected in a no negligible proportion by the existence of an enhanced (contaminated) background due to the previous treatment of Morocco material.
- 3) It is necessary to highlight that the values compiled in Table 5 explicitly correspond to the increments in the external *absorbed* gamma dose rates determined inside the factories. In order to evaluate the increments in the *effective* doses received at each location by the workers through this pathway, the corresponding occupational factor need to be taken into account. Taken a maximum and quite improbable value of 0.23 for this occupational factor (implies the presence of the worker of 8 hours per day, 5 days per week and 50 weeks per year) increments of the effective doses clearly lower than 0.3 mSv/year would be received by them in the majority of the monitored places due to external radiation. Only in the filtration zone, and more specifically, above the filter, the increment of effective doses due to external radiation would be higher with the assumed pessimistic occupational factor, but in this particular case, and as it is indicated in Table 5, the aforementioned zone is not accessible (or accessible sporadically) for the workers. It can be then concluded that under normal running operations the increments in the effective doses

received by the workers inside the analysed facilities due to external radiation are clearly lower than 1 mSv/year.

Table 5. Increments of the external gamma dose rates (mGy/y) over background, registered at several points inside the facilities when Morocco and Kola phosphate rocks were processed. The relative uncertainties of the measurements are in the range 5-10%.

External gamma dose rates (mGy/y) inside the factories above background	Morocco	Kola
<i>Fertiliser stores</i>		
Inside a DAP store	0.25	0.25
<i>Milling zone</i>		
Inside phosphorites silo	2.20	0.60
1 meter beside silo	0.35	1.50
1 meter away milled rock pile	0.40	--
Mill operator cabin	0.25	0.45
1 meter away rock dust pipes	0.80	--
<i>Reaction zone</i>		
Above compartments 3 and 4 of reactor	0.90	0.95
At 2 meters of compartments 4 and 5 of reactor	0.10	--
Above compartments 4 and 5 of reactor	0.10	0.45
<i>Filtration zone (above the filter, not accessible to the workers)</i>		
At 1 meter between the pulp entrance and the 1 st washing	6.75	4.20
At 1 meter of the 1 st washing	9.20	8.95
At 1 meter between the 1 st and 2 nd washing	6.40	4.90
At 1 meter of the 2 nd washing	8.65	9.90
<i>Filtration zone (around the filter, accessible to workers)</i>		
Between the pulp entrance and 1 st washing	1.50	1.05
Between the 1 st and 2 nd washing	1.50	1.20
Between the 2 nd and 3 rd washing	1.05	1.05
<i>Concentration zone</i>		
At 2 meters of the concentration zone	0.10	--
Above the production acid decantation pool	1.85	--
<i>Other places</i>		
Chemical laboratory	0.00	0.00
Control process room	0.10	0.00
Old control process room	0.00	--

- 4) It is important to bear in mind that the dosimetric discussion done in the previous paragraph, has been done considering only the effects related to external radiation. Additional studies are now under progress for the estimation of the possible increments in the effective doses received by the workers due to inhalation of particulate matter and radon. In addition, it needs to be remarked that the shown dosimetric determinations have been carried out under normal running conditions of the factories. No specific measurements have been done until now during maintenance and cleaning operations of the pipes, deposits and other components of the installations.

5. Occupational exposures in the phosphogypsum deposits

As it was stated in the introductory section of this paper, the great majority of the huge amounts of phosphogypsum produced in the Huelva factories have historically been stored in a surrounding salt-marsh area (this area can be seen in the Figure 1, at the top of the picture). The phosphogypsum has been transported there after its mixing with water by pumping. During 30 years, the transported phosphogypsum was accumulated by decantation forming piles while the waters used to its transportation drained to the estuary. This management policy had an obvious consequence: the strong and unambiguous contamination of the estuary with natural radionuclides and other stable elements, contamination, which was increased due to the direct release of a fraction of the phosphogypsum produced by one of the factories to the estuary [3, 10]

Since 1998, and following the instructions given by the regional government, the management policy followed by the industries in the storage of phosphogypsum has changed drastically. The phosphogypsum continues being stored in the aforementioned salt-marsh area, but several countermeasures were taken to minimise the interaction between the piles and the neighbouring estuary waters. From 1998, the phosphogypsum is transported to the storage area through a closed circuit, in such a way that the waters used for its transport from the factories to the storage area recirculates, coming back to the factories for the transport of new generated phosphogypsum. In addition, the drainage of some water from the piles to the estuary was avoided by the construction of a perimetral channel, which collects them. These collected waters are also reintroduced in the closed circuit.

By this way, an enormous pyramidal pile of phosphogypsum is being formed. It is expected that this pile accumulates all the phosphogypsum to be produced by the factories until 2010.

In the management and construction of this pyramidal phosphogypsum pile are involved several workers of the factories, which devote to these activities a fraction of their working time. Being this storage area a clear radiological anomaly [11, 12] since the phosphogypsum accumulated in the pile (mostly produced after the treatment of Morocco rocks) is enriched in several radionuclides, especially ^{226}Ra , it is clear that the radiation exposures of the previously cited workers need to be evaluated.

In this direction, a set of external absorbed gamma dose rate measurements were performed in different points of the storage zone where nowadays the workers are performing their activities. These measurements were carried out with the monitor previously used inside the factories with the same objective, and at each point each measurement (1 minute) was replicated five times in order to achieve a representative average value.

The results obtained in these determinations are compiled in Table 6, and have been detector-noise and cosmic ray corrected. In addition, the soil background (0.40 mGy/y) [11] was also subtracted to arrive to these values. Consequently, we can indicate more precisely that the results in Table 6 represent the increments over background in the external absorbed gamma dose rates that could be received by the workers in the analysed points of the phosphogypsum storage area.

Table 6. Enhancements of the external gamma dose rates (mGy/y) over the background, registered at several points of the pile used nowadays for the storage of the phosphogypsum produced in the Huelva factories.

Point	External gamma dose rate (mGy/y) above background	Point	External gamma dose rate (mGy/y) above background
1	2.69	10	1.20
2	1.23	11	1.24
3	1.05	12	1.06
4	2.13	13	1.38
5	1.31	14	1.47
6	1.31	15	1.38
7	1.63	16	1.51
8	1.08	17	1.25
9	1.52	18	0.85

From these values, and assuming a quite realistic occupation factor of 0.10, it can be immediately deduced that the workers involved in the maintenance and construction of the pyramidal phosphogypsum pile received an additional effective dose due to external radiation, which is lower than 0,3 mSv/y.

The aforementioned additional effective dose received by the workers handling their activities in the phosphogypsum storage area, only represents a minor increment if we have in consideration the extra contribution due to inhalation of particulate matter. A sampling campaign, still running, collecting air filters at 1 m height in several points of the piles, has allowed the estimation of the particulate concentrations in the air susceptible to be inhaled by the workers, as well as of the amount of the different natural radionuclides incorporated by them through this pathway. The set of results obtained until now, has conducted to a preliminary estimation, indicating that the additional effective dose through the inhalation of particulate matter is lower than 10 µSv/y.

The dosimetric study as a whole was finished by the estimation of the additional effective doses caused by the possible inhalation by the workers of enriched concentrations of ^{222}Rn . A priori, could appear some concern about the magnitude of the additional effective doses through this pathway, since huge amounts of ^{226}Ra are accumulated in the storage area, inducing the emanation of elevated amounts of ^{222}Rn . Nevertheless, ^{222}Rn concentrations determinations carried out in the storage area, still under progress, indicates their negligible increase in relation with the values determined in background zones of the region. In fact, an average ^{222}Rn concentration value of $13.1 \pm 1.6 \text{ Bq/m}^3$ was obtained during a monitoring period of six months in the storage area, while the average ^{222}Rn concentration value in the background zone (few km away from the phosphogypsum pile) was $12.6 \pm 2.0 \text{ Bq/m}^3$. The obtained values are then reflecting the quick and ample dilution of the radon emanated from the piles in the neighbouring atmosphere.

We can then conclude this section indicating that the additional effective doses susceptible to be received by the workers carrying out their activities in the maintenance and construction of the pyramidal phosphogypsum pile are clearly lower than 1 mSv/y.

6. Conclusions

In this work, the distribution of several natural radionuclides along the industrial process followed in phosphoric acid production Spanish factories has been analysed. The gained knowledge in the aforementioned study has served as basis for the design and performance of dosimetric campaigns in order to evaluate the occupational exposures of the workers that carry out their activities inside the factories and in the storage area of the generated by-products. Although these campaigns are still in progress, the available results indicate that the additional effective dose rates susceptible to be received by the workers devoted to the maintenance of the storage area are clearly lower than 1 mSv/y (considering external radiation, inhalation of particulate matter and inhalation of radon as the main pathways contributing to these doses), while under normal running conditions the limit of 1 mSv/y is also not reached by the workers handling their activities inside the factories due to external radiation. In the last case, the estimation of possible additional dose rates due to inhalation of particulate matter and radon are under study.

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