1 **BEHAVIOUR AND FLUXES OF NATURAL RADIONUCLIDES IN THE PRODUCTION**

2 **PROCESS OF A PHOSPHORIC ACID PLANT**

3

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8

9 **ABSTRACT**

10

11 In recent years there has been an increasing awareness of the occupational and public hazards of the

12 radiological impact of non-nuclear industries which process materials containing naturally

13 occurring radionuclides. These include the industries devoted to the production of phosphoric acid

14 by treating sedimentary phosphate rocks enriched in radionuclides from the uranium series.

15

16 With the aim of evaluating the radiological impact of a phosphoric acid factory located in the south-

17 western Spain, the distribution and levels of radionuclides in the materials involved in its

18 production process have been analysed. In this way, it is possible to asses the flows of radionuclides

19 at each step and to locate those points where a possible radionuclide accumulation could be

20 produced. A set of samples collected along the whole production process were analysed to

21 determine their radionuclide content by both alpha-particle and gamma spectrometry techniques.

22 The radionuclide fractionation steps and enrichment sources have been located, allowing the

23 establishment of their mass (activity) balances per year.

24

25

26

1 **1. Introduction**

2 *1.1. Background*

3 Several phosphate processing plants are located on the southwestern coast of Spain (on the outskirts

4 of the town of Huelva), close to the estuary of the Odiel and Tinto rivers, where phosphoric acid has

5 been produced since 1968. The company imports sedimentary phosphate ore (Phosphate Rock)

6 containing around 100-150 ppm of uranium, which mainly comes from Morocco (Bolivar et al.,

7 1996a). The phosphate is treated (dissolved) at these plants by mixing it with sulphuric acid to

8 produce phosphoric acid by the di-hydrate process. A by-product called phosphogypsum (mainly

9 calcium sulphate), is also produced during this process.

10

11 Until 1998, about 20 % of phosphogypsum produced annually was discharged into the sea. The

12 remaining 80 % was pumped in suspension with sea water (20 % phosphogypsum + 80 % seawater)

13 and subsequently transported about 2 km away the factories, to be disposed in large piles located in

14 a salt-marsh area along the Tinto river estuary. Until 1997, the sea water used for this transportation

15 was discharged into the estuary where the phosphogypsum piles were formed. At the start of 1998,

16 direct discharges into the sea were banned following the OSPAR convention (OSPAR 1996), with

17 all the phosphogypsum stored in a pile in the town's surroundings. The fresh water used for its

18 transportation had to follow a closed circuit in order to avoid any impact on the estuarine ecosystem

19 (Absi et al., 2005; Mas et al., 2006). Nowadays, a small fraction of the phosphogypsum produced

20 (less than 10 %) is used in agriculture as soil amendment for sodic soils (El-Mrabet et al., 2003).

21

22 The process for obtaining the phosphoric acid from the phosphate rock can be described

23 schematically by the following chemical reaction (Fertiberia, 2002):

24

25 $$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4 + 48.9\ kcal$$
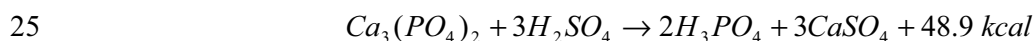
26

1 This reaction is exothermic and its magnitude is self-limited due to the formation of an insoluble

2 layer of calcium sulphate over the phosphate particles. To avoid this self-limitation, a high

3 recirculation of the produced phosphoric acid is imposed to favour the conversion of phosphate rock

4 in mono-calcium phosphate. Then, it reacts with the sulphuric acid to produce the phosphoric acid

5 required:

6

7
$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$
$$3Ca(H_2PO_4)_2 + 3H_2SO_4 \rightarrow 6H_3PO_4 + 3CaSO_4$$
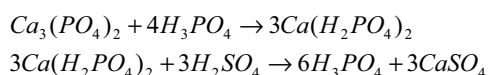
8

9 The phosphogypsum (insoluble calcium sulphate) is separated from the phosphoric acid by

10 filtration. Phosphogypsum can be obtained in different crystalline forms depending on the

11 temperature, concentration of the phosphoric acid and the amount of free sulphuric acid in the

12 digesters (Rutherford et al., 1994). In the Huelva phosphoric acid plants, the process conditions

13 induce the production of the phosphogypsum in the di-hydrate form, according to the following

14 general reaction (Fertiberia, 2002):

15

16 $$Ca_{10}(PO_4)_6F_2CO_3Ca + 11H_2SO_4 + 21H_2O \rightarrow 6H_3PO_4 + 11CaSO_4 \cdot 2H_2O + 2FH + CO_2$$
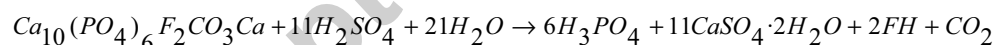
17

18 In the Huelva phosphoric acid plants, around 1.5 millions tonnes of phospate rock are treated

19 annually, and some 500,000 tonnes of phosphoric acid and 2.5 million tonnes of phosphogypsum

20 are produced. Phosphogypsum is an unavoidable by-product in the production of phosphoric acid

21 by the sulphuric "wet-acid" method, formed in the proportion 5-6 Tonnes of phosphogypsum per

22 Ton of P_2O_5 produced

23

24 *1.2. Detailed description of the process*

1   The process for the phosphoric acid production from Moroccan phospate rock is identical in all the

2   plants in Huelva. For that reason, all the studies in this paper will concentrate on just one of the

3   plants. The industrial process can be divided in four different steps: 1) grinding and conditioning of

4   the phospate rock, 2) attack, or digestion, of the phospate rock with sulphuric acid, 3) filtration, or

5   phosphogypsum separation from the liquid fraction of phosphoric acid, and 4) washing of

6   phosphogypsum by water. The phosphoric acid produced has a P_2O_5 concentration of 27 %, which

7   later rises to 54 % through a concentration step by evaporation of a fraction of its water content.

8

9   Figure 1 shows schematically the process used in the step of conditioning and grinding of the

10   phospate rock (step 1). The commercial phospate rock (transported to the factory by ships with a

11   granulometry in the range 0- 2 mm) is stored initially in big silos. Then it is taken and transported

12   by hoppers, which feed a ball mill where the grain size of phospate rock is reduced until 90 % of the

13   grinded material has a size less than 147 μm and 60 % less than 74 μm. Finally, the grinded

14   material is transported by an ascendant air current of several cyclones, which discharge it in another

15   hopper that feeds the digesters where the phospate rock is attacked.

16

17   Figure 2 shows schematically the process used in the acid attack on the phosphate rock (step 2). In

18   this phase of the process, the grinded phosphate rock is dissolved with sulphuric acid diluted to a

19   concentration of 60 % with water. This water is mostly fresh water coming from outside the factory,

20   although a small fraction originates in the process (deposit A, see figure 2).

21

22   The reaction of the phosphate rock with the sulphuric acid takes place in a reactor of seven

23   compartments where the temperature is maintained at 70-75 ºC. To improve the chemical reaction,

24   some phosphoric acid, 22 % obtained in the filtration step (step 3), is added, coming back through

25   the process. The pulp produced in the reaction is continuously mixed and circulates from

26   compartment 1 to compartment 5. Then it passes to a flash cooler where its temperature decreases

1   and the dissolved gases are removed (the flash cooler works in vacuum conditions and the gases are

2   condensed in a condenser with the help of water previously used in the management-disposal of the

3   phosphogypsum). Once the pulp is cooled, it is transported to compartment 7 of the reactor (see

4   Figure 2), from where it is transported to the filtration process through the reactor 6 (step 3). The

5   water used in the condensation of the gases produced in the reaction is stored in deposits A and B

6   (see Figure 2) to be later reused during the process. In deposit B, water which has previously been

7   used in the management-disposal of phosphogypsum is also stored.

8

9   In Figure 3, the process used for the filtration of the pulp produced in the digestion step (step 3) and

10   phosphogypsum washing (step 4) is shown schematically. In this filtration process, the phosphoric

11   acid is separated from the phosphogypsum using a rotating filter system formed of 24 independent

12   filtering trays which can tilt to discharge the phosphogypsum after its filtration and washing. The

13   rotating system (rotation along a vertical axis which is perpendicular to the trays) has a total

14   filtration area of 69 m^2, and takes around 3 minutes to rotate 360º. The separation and washing step

15   is performed through filtering clothes, covering the surface of the trays, by the vacuum generated by

16   two large vacuum pumps.

17

18   The pulp coming from the reactor is placed on the trays, and in a first small suction (called "pre-

19   suction") 27 % P_2O_5 is extracted and stored in Deposit W (see Figure 3). A second suction separates

20   the production acid (27 % P_2O_5) which is sent to Deposit X (see Figure 3). Afterwards, the washing

21   step of the pulp remaining on the filter starts (formed mostly by phosphogypsum). Three successive

22   washings are used in order to extract the remaining phosphoric acid still in the phosphogypsum.

23

24   The first washing is carried out with PA at 12 % P_2O_5 where phosphoric acid with 22 % P_2O_5 is

25   obtained and stored in Deposit W. The second washing is done with 5 % P_2O_5 to produce 12% P_2O_5

26   which, after storage in Deposit Y (see Figure 3), is used in the first washing. Thirdly, a final

1 washing is performed with hot water from Deposit C (see Figure 3) to produce 5 % P_2O_5, which is

2 used in the second washing following storage in Deposit Z (see Figure 3).

3

4 Once the washings have finished, each tray rotates 180º and discharges the phosphogypsum over a

5 ramp to be mixed with water coming from the phosphogypsum piles (Deposit B, see figure 2) in

6 Tank D. From this tank, the phosphogypsum -water mixture is sent to the phosphogypsum piles for

7 the storage of this by-product. The filtration process finishes with the washing of the filter clothes

8 using hot water (which is collected as waste water along the plant) from Deposit B. Such water is

9 later stored in Deposit C to be used in the third washing step, and by rotating the tray back to its

10 original position to start a new filtration cycle.

11

12 These suctions and washings are essential to obtain a high efficiency phosphoric acid in the

13 filtration process. The objective is to obtain a phosphogypsum with a P_2O_5 content less than 0.5 %,

14 before it is sent to the storage stacks (Becker, 1989). In summary, phosphoric acid extracted in this

15 filtration process is stored in four deposits. The deposits Y and Z contain 12% and 5% P_2O_5,

16 respectively, which is used in the same filtration process for washing the pulp. Deposit W contains

17 22 % P_2O_5 to be used in the reactors to improve the reaction of the phosphate rock with the

18 sulphuric acid (see Figure 2). Finally, deposit X contains 27 % P_2O_5 (production acid) which is sent

19 to a final step of concentration for obtaining commercial acid (54 % P_2O_5).

20

21 Indeed, the 27 % P_2O_5 produced in the filtration step should be concentrated up to 54 % (step 5),

22 since it is the normal concentration needed for the fabrication of the most demanded phosphate

23 fertilisers: Monoamonium Phosphate (MAP), Diamonium Phosphate (DAP), and complex fertilisers

24 (NPK). This concentration process is a pure physical process, and is carried out by the removal of

25 water by evaporation in vacuum. This vacuum is performed by using powerful vacuum pumps

26 (reaching up to 60 mm Hg).

1

2 The system used since 1998 for the disposal of the phosphogypsum produced in the Huelva plants

3 is shown in Figure 4. The phosphogypsum is now piled in a site having about 170 ha of surface.

4 The piling system consists on: a) two ponds for the decantation and storage of the phosphogypsum,

5 covering an area of 150 ha, b) a regulatory reservoir with an area of 17 ha, and c) a perimetral

6 channel to collect all the filtrations (or leachings) from the piles. The process follows a closed

7 circuit: the water used for the transport of the phosphogypsum is firstly clarified in the ponds due to

8 the decantation of the phosphogypsum and cooled in contact with the atmosphere. Afterwards, it

9 goes to the regulatory reservoir before being returned to the phosphoric acid plants for use in the

10 transport of new phosphogypsum. Thus, the possible contamination of the natural aquatic

11 ecosystem that surrounds this storage area is minimised.

12

13 Two independent lines (pipes) are used in Huelva for the transport of the phosphogypsum mixed

14 with water to the ponds. Two additional lines for returning the clarified water to the plants are also

15 used. This transportation is carried out with the help of several pumps. The phosphogypsum stored

16 after the filtration process in Deposit D mixed with water is conditioned to obtain a solution having

17 17-22% weight of suspended matter and a temperature of 50ºC. From there, it is transported to the

18 ponds (with a flow rate of 1,400 m^3/h). The flow of the clarified and cooled water to the plants is

19 lower (900 m^3/h) due to losses by evaporation and filtration.

20

21 In order to operate properly following a closed circuit, it is necessary to cool the water to 27 ºC

22 before its return to the plants, because at this temperature the water can be used at different stages

23 of the production process. In addition, it is necessary to highlight the importance of the regulatory

24 reservoir, which absorbs the possible oscillations in the water level of the ponds due to heavy

25 precipitation, storage or evaporation. This regulatory reservoir can even absorb oscillations of 0.5

26 millions of cubic meter in the water level.

1

2 Each of the two storage ponds allows the homogeneous distribution and subsequent discharge of the

3 decanted phosphogypsum. The objective is to construct a steeply pyramidal pile with a height of 30-

4 35 m, covered by a soil layer of 0.5 m thickness which allows the fixation of vegetation for the

5 integration of these piles into the neighbouring environment.

6

7   *1.3. Aims and objectives*

8 It is well known that huge amounts of natural radionuclides belonging mainly to the uranium decay

9 chain are involved in the so-called "wet-acid" process of phosphoric acid production, which has a

10 notable impact on the environment (Bolivar et al., 1996a,b, 2002; Aguado et al., 2004; Betti et al,

11 2004). This fact has aroused an awareness of the occupational and public hazards of the radiological

12 impact of this type of non-nuclear industries (IAEA, 2007).

13

14 The aim of this investigation has been to study the fluxes and behaviour of these natural

15 radionuclides throughout the production process of a phosphoric acid plant in southwestern Spain.

16 This work intends to understand the behaviour of radionuclides (U, Ra, Th, Pb, Po) in this industrial

17 process, being this an essential step in the evaluation of the occupational effective doses received by

18 the working staff. The evaluation and analysis of the occupational doses determined in the plant are

19 currently under analysis. The study of their correlation with the radionuclide determinations

20 performed during the process will be presented in the second part of this research.

21

22 **2. Materials and Methods**

23   *2.1 Samplings*

24 After an exhaustive analysis of the production process, the sampling points were selected and the

25 radiological assessments were performed. The amount of material in each sampling point was about

26 1 kg for a solid sample, and 5 kg for liquid or pulp material. A higher mass for liquid/pulp fraction

1 was necessary in order to guarantee that enough mass of this fraction was available for replication

2 (if required) after water removal. The sampling was carried out when Moroccan sedimentary

3 phosphate rock material was processed.

4

5 The description of the samples collected during the process is compiled in Table 1. These samples

6 have been classified according to the step of the process from which they were collected: 1) milling

7 and grinding, 2) acid attack or digestion, 3) filtration and washing, and 4) concentration. The

8 location of the collection for most of the samples is also indicated in Figures 1, 2 and 3. These

9 samples are identified by the code X-n, where "X" indicates the step of the process where they were

10 collected (M = Milling, A = Attack, F = filtering and washing, C = concentration), and "n"

11 represents the order number of each sample.

12

13 In addition, six water samples from the regulating reservoir associated to the big pile (where the

14 phosphogypsum is stored) have been sampled and analysed. This water is used for the

15 phosphogypsum pumping into the ponds, and it was collected over a year at a rate of one sample

16 per two months in order to evaluate the temporal evolution in its radionuclide content.

17

18 *2.2 Sample preparation*

19 The samples collected in the industrial process were either liquids (acids, water), solids (PR,

20 phosphogypsum), or cakes formed by a mixture of phosphoric acid, phosphogypsum and other

21 unknown solid materials. The liquid samples were filtered (pore size 0.8 µm) before their analysis.

22 The solid samples were first dried at 60 ºC, in order to avoid the loss of the hydration water in the

23 phosphogypsum samples, and afterwards homogenised mechanically, grinded and passed through a

24 0.8 mm sieve. For the cake samples, the liquid and solid fractions were separated by different

25 methods (centrifugation, filtration under vacuum), with the liquid fractions finally passing through a

1 filter with a 0.8 µm pore size. After separation, the solid fractions were conditioned following the

2 same protocol used for the solid samples.

3 **2.3 Radionuclide determinations**

4 *Gamma-ray spectrometry*

5 Aliquots of the pre-treated and conditioned samples were introduced into polypropylene cylindrical

6 containers with a diameter of 6.6 cm, up to a height of 5 cm for analysis by gamma-ray

7 spectrometry.

8

9 The gamma-ray determinations were performed with a coaxial hyper-pure Ge detector (Extended

10 Range (XtRa) type, model GX3519 from Canberra industries), mounted with a carbon window of

11 0.5 mm thickness, relative efficiency of 38.4%, and FWHM of 0.95 keV at the 122 keV line of

12 ^{57}Co and 1.9 keV at the 1333 keV line of ^{60}Co. The detector is connected to a conventional

13 electronic chain, including a multichannel analyser, and is shielded by Fe 15 mm of thickness. The

14 detector with its shielding is located in a room with walls and ceilings made of 75 cm-thick concrete

15 on the ground floor of a four-storey building in order to minimize the natural background of the

16 measuring system.

17

18 For gamma-ray quantitative determinations, we have developed an original efficiency calibration

19 procedure in the energy range of 150-1800 keV (Perez-Moreno et al., 2002). It takes into account

20 the self-absorption differences between the problem sample and the calibration sample. ^{226}Ra

21 activities were determined by the 352 keV emission of ^{214}Pb. Both nuclides were in secular

22 equilibrium since counting was done at least one month after filling and sealing the cylindrical

23 container. ^{228}Ra determination was carried out by the emission of 911 keV of ^{228}Ac, while ^{228}Th was

24 determined by the 583 keV photon of ^{208}Tl taking into account the branching ratio in the decay

25 scheme of these nuclides. On the other hand, ^{210}Pb activities were also determined from the same

1   measurement by using an independent efficiency calibration which was performed specifically by

2   the of 46.5 keV photon emitted by this radionuclide (Bolivar et al., 1994; San Miguel et al., 2002).

3

4   *Alpha-particle spectrometry*

5   Aliquots of around 5 g in the case of acids and solids, and about 1 L in the case of waters were

6   taken for the determination of several alpha-emitters by alpha-particle spectrometry. U-isotope

7   (^{238}U, ^{235}U, ^{234}U) and Th-isotope (^{232}Th, ^{230}Th) mass activities were determined by alpha-particle

8   spectrometry. To this end, a sequential well-established radiochemical method was applied to

9   representative aliquots of the samples (Holm and Fukai, 1977). In this method, the U-isotopes and

10   the Th-isotopes once isolated are electrodeposited onto stainless steel planchets (Hallstadius, 1984).

11   Typical recoveries of 60-80 % for uranium and 50-70 % for thorium were obtained.

12

13   **3. Results and Discussion**

14   ***3.1 Natural Radioactivity concentrations throughout the process***

15   Radionuclide concentrations of the samples collected throughout the P_2O_5 production process are

16   shown in Table 2 (milling and digestion steps), and in Table 3 (filtration, washing and concentration

17   steps). Additionally, in Table 4 the most interesting activity ratios for the most representative

18   samples analysed are compiled.

19

20   As can be seen from Table 2, the phosphate rock treated for the production of phosphoric acid is

21   clearly enriched in radionuclides from the uranium series. Their concentrations are in line with data

22   from the Moroccan sedimentary phosphate rocks found in literature (Azouazi et al., 2001). They are

23   also at least 50 times higher than in representative unperturbed soils worldwide (UNSCEAR, 2000).

24   In addition, it is possible to observe that all members of the uranium series are in secular

25   equilibrium (see Table 4, sample M-3), as expected due to the fact that the material does not

26   experiments any radionuclide enrichment during the physical processes applied before digestion.

1   On the other hand, the activity concentrations of the radionuclides belonging to the ^{232}Th chain in

2   the treated phosphate rock are quite reduced (see, for example, ^{232}Th/^{238}U activity ratio of sample

3   M-3, Table 4). For this reason the discussion of these nuclides will be fairly limited in this paper.

4

5   During the digestion step, we observe the first clear evidence of different behaviour that the

6   analysed radionuclides from the U-series show in the process. It is possible to observe a non-

7   homogenous, varied distribution of the analysed radionuclides between the liquid and solid

8   fractions in the pulp samples collected from the digesters. The liquid fractions, corresponding

9   mainly to the phosphoric acid formed at this step, are clearly enriched in uranium, whilst the

10   concentrations of ^{230}Th, ^{226}Ra, and ^{210}Pb are evidently lower or even negligible (this is the case of

11   ^{226}Ra). On the contrary, solid samples contain the major proportion of the ^{230}Th, ^{226}Ra and ^{210}Pb

12   originally present in the phosphate rock, while the uranium isotopes concentrations are slightly

13   lower (but far from negligible, see activity ratios of sample A-4S, Table 4). This solid fraction is

14   mostly composed of the phosphogypsum formed in reaction to the phosphate rock with sulphuric

15   acid. However, it may also contain a proportion of non-attacked phosphate rock and some

16   phosphoric acid occluded between the phosphogypsum grains and not separated from the liquid

17   samples.

18

19   For a better understanding of the previously mentioned results, it is necessary to take into

20   consideration the main three inputs of radionuclides from the uranium series to the digestion step. In

21   addition to the main input associated to the treated phosphate rock, significant amounts of 22 %

22   P_2O_5 are used in order to favour digestion, and furthermore some amounts of water for dilution of

23   the sulphuric acid are used for attacking the rock. The last two sources contain enhanced amounts of

24   radioactivity (see Table 2). Indeed, the 22% P_2O_5 is clearly enriched in Uranium isotopes, with

25   clearly lower concentrations of the other radionuclides determined from the uranium series. This

26   finding is in good agreement with the results obtained in the liquid phases of the pulp, as expected,

1   while the water fed into the digester (sample A9) is also particularly enriched in uranium. This

2   water is formed by a mixture of freshwater and recycled water. The freshwater (sample A8) comes

3   from a reservoir near the factories and contains negligible amounts of radioactivity. The recycled

4   water (samples A6 and A7), which is used previously for the transport of phosphogypsum to

5   storage, contains particularly elevated amounts of Uranium. Consequently, the input of the uranium

6   isotopes in the digestion step is clearly higher than that associated to the mineral feeding the

7   process. On the contrary, the additional inputs in the case of analysed uranium daughters (^{230}Th,

8   ^{226}Ra and ^{210}Pb) are negligible.

9

10   The results obtained in the analysis of the samples collected in the filtration step allowed the

11   confirmation of the different behaviour of the Uranium isotopes and their daughters previously

12   drawn. By observing the data shown in Tables 2 and 3, we can affirm that most of the uranium

13   tends to be associated to the phosphoric acid fraction, while the majority of ^{230}Th, ^{226}Ra and ^{210}Pb

14   tends to be associated to phosphogypsum. These conclusions are evident by observing the obtained

15   activities in the phosphoric acid samples. They present high values of U-isotopes and clearly lower,

16   or negligible, concentrations of their daughters. The concentration of U decreases in the

17   phosphogypsum samples according to their successive washings, a fact indicating that the amounts

18   of P_2O_5 that remain associated to the gypsum are removed sequentially in the different washings.

19   Consequently, the uranium associated to this acid is removed. On the contrary, the concentrations of

20   ^{230}Th, ^{226}Ra and ^{210}Pb remain inalterable in the successive washings because these radionuclides

21   cannot be found associated to the acid fraction.

22

23   Due to the extremely close association of the uranium with the liquid fractions containing P_2O_5, it is

24   even possible to observe a clear correlation between the concentrations of this element and the

25   strength of the phosphoric acid samples analysed from the filtration area (Figure 5).   This

26   correlation is even closer if we also include the phosphoric acid samples collected in the final

1   concentration step. This is due to the fact that these last samples only suffer the loss of a fraction of

2   their water content by evaporation. As a consequence, they experience an increase in their uranium

3   levels by concentration following strictly the increase in their P_2O_5 percentage.

4

5   Both good correlation coefficient and acceptable uncertainties for fit parameters were obtained.

6   These facts are thus supporting the affinity of uranium fraction for the phosphoric acid fraction.

7   Bearing in mind that this acid is used for phosphate fertilizer production, such an accumulation is in

8   agreement with the well reported accumulation of uranium in fertilizers (Yamazaki and Geraldo,

9   2003; Saueia and Mazzilli, 2006). On its turn, the use of fertilizers with high P_2O_5 contents could be

10 the origin of a certain accumulation of this element on tilled soils (Rothbaum et al., 1979).

11

12 On the contrary, observing this correlation is however more difficult for the uranium daughters due

13 to their low affinity with the P_2O_5. However, it is necessary to indicate that the behaviour is not

14 exactly the same for all the uranium daughters analysed. While the concentrations of [226]Ra are

15 negligible in the P_2O_5 fractions, the levels of [230]Th and ^{210}Pb in these samples are clearly higher. In

16 fact, by ordering all the analysed elements according to their affinity to the phosphoric acid, we can

17 indicate that:

18

19   U-isotopes >>> [230]Th > [210]Pb > [226]Ra

20

21 The uniformity in the [226]Ra, [230]Th and ^{210}Pb concentrations in the gypsum samples collected in the

22 process (regardless of the number of washings applied) is in opposition to the behaviour of the

23 uranium isotopes. This finding indicates that the uranium daughters are strongly bound to the

24 gypsum matrix, and their concentrations in liquid fractions will be driven by dilution factors in

25 relation to the mass percentage P_2O_5. These facts can explain the results obtained in the water used,

26 first for the transport of this by-product to the disposal site, and afterwards in the process after its

1   recirculation (samples A6, A7 and F9). As previously mentioned, this water is especially enriched

2   in the uranium isotopes while it presents clearly lower concentrations of the uranium daughters,

3   which tend to remain bound to the solid gypsum material (see activity ratios, Table 4). Laboratory

4   leaching experiments were performed by our group using phosphogypsum collected at the Huelva

5   factory just before mixing with water and transportation to the phosphogypsum ponds. The results

6   confirm the previous comments (Aguado et al., 2005).

7

8   The high radioactive content (specially in uranium) of the water used for the transport of the

9   phosphogypsum to the disposal area needs to be considered in a construction of the radionuclide

10   balances in the processes due to their recirculation and active use in the process. The radioactive

11   content of this water is fairly uniform over time. This fact can be deduced from the analysis

12   performed on 6 aliquots from different locations in the reservoir associated to the piles where the

13   phosphogypsum is stored (see Table 5). As previously explained, these samples were collected over

14   one year and at a rate of one sample per two months. The data shown in this Table should be

15   compared with the results obtained in the samples A6, A7 and F9 (Tables 2 and 3,) which also

16   correspond to waters used for the transport of the phosphogypsum but collected after returning to

17   the plant.

18

19   *3.2 Mass and radionuclide balances in the process*

20   In Figure 6, the scheme of the global production process applied in obtaining phosphoric acid by the

21   wet acid method in the Huelva production plant analysed in this work is shown. The most

22   representative sampling points for the mass-balance and radionuclide fluxes are marked by solid

23   frames. The frames with dashed lines correspond to samples with marginal entity inside the process.

24   These mass and radionuclide activity balances have been performed with the objective of

25   confirming clearly the main routes followed by the different radionuclides of the uranium series

1   involved in the process. They also help to the evaluation of the magnitude of the possible emissions

2   of natural radioactivity into the environment.

3   In Figure 7, the mass balance in the P_2O_5 production process corresponding to the analysed plant is

4   shown in graph form. The data have been normalised to the amount of Moroccan phosphate rock

5   introduced into the process, which is 44 Tonne per hour. In the elaboration of this mass balance, the

6   following losses throughout the process have been considered: a) 1 Tonne per hour in

7   phosphogypsum and 3 Tonne per hour in acids in the filtration step, which represents 1 % of the

8   phosphogypsum produced and 8 % of the liquids used in the washings, b) 2 Tonne per hour of pulp

9   in the reaction step, and c) 2.8 Tonne per hour of CO_2 by evaporation and 6.9Tonne per hour of F in

10   the form of H_2SiF_6 also in the reaction step.

11

12   All the data shown in Figure 7 correspond to the average values determined in a typical month of

13   production at the plant. It can be deduced that for every Tonne per hour of phosphate rock attacked

14   (sample M3), 1.11 Tonne per hour of production phosphoric acid (27 % P_2O_5, sample F2) and 1.97

15   Tonne per hour of phosphogypsum containing approximately 20 % in weight of water (sample F11)

16   are produced. In addition, the consumption of water in the plant includes 0.60 Tonne per hour used

17   in the dilution of the sulphuric acid prior to its reaction with the phosphate rock in the digesters,

18   1.06 Tonne per hour used in the washing of the filters, and 0.03 Tonne per hour associated to the

19   humidity of the phosphate rock and to the water content of the concentrated sulphuric acid.

20

21   The mass-balance study showed and discussed previously has been the basis (together with the data

22   compiled in Tables 2 and 3) for the quantitative elaboration of the fluxes of the radionuclides from

23   the uranium series involved in the process.

24

25   In Figure 8, the normalized flux of radioactivity associated to [238]U is presented. The normalization

26   was performed on the uranium content introduced in the process associated to the phosphate rock.

1   As previously explained, the ^{238}U is introduced with the phosphate rock (sample M) and the water

2   used in the washing of the phosphogypsum (sample F9). Its activity is distributed between the

3   production phosphoric acid (sample F2) in a proportion of 51 % and the phosphogypsum (41 %). So

4   it can be concluded that the uranium has the tendency to stay in dissolution in an acidic medium.

5   This conclusion is also reinforced if we consider that a fraction of the uranium detected in the

6   phosphogypsum is associated to the acid liquid where it remains. This finding can be deduced in

7   two ways. First, observing the uranium enrichment in the water of the process (F10) after the

8   washing of the filters used for separation of the phosphogypsum, to give the water F9. Second,

9   observing the uranium content in the waters used for the transport of the phosphogypsum to the

10   storage area. In fact, the acid water returning to the plant after the transport of the phosphogypsum

11   to the disposal area contains around 65% ^{238}U in the amount bound to the phosphate rock.

12

13   Quantitatively, we can indicate the ^{238}U activity input rates: 76 MBq/h associated to the phosphate

14   rock, 14.1 MBq/h associated to the water used for the washings in the filtration area, and 48.4

15   MBq/h associated to the water returning from the disposal area. Furthermore, the amount of this

16   nuclide leaving the process in the filtration step associated to the production phosphoric acid (27%

17   P_2O_5), is 54.9 MBq/h. Finally, 99.9 MBq/h of ^{238}U leaves the process with the mixture of water and

18   gypsum transported to the piles. Consequently, it is possible to affirm the existence of agreement

19   between the inputs and outputs of Uranium in the process (with a lower deviation of 10 %). The net

20   annual flux of ^{238}U sent to the piles for its disposal from the plant is 0.42 TBq per year.

21

22   In Figure 9, the normalized flux of radioactivity associated to ^{230}Th is shown. In this case, the

23   phosphate rock is the only significant source of this nuclide in the production process because the

24   ^{230}Th content of the water involved in the process is very low according to the mass-balance

25   obtained. This result is compatible with the very low solubility of this element in water regardless

26   of its acidity (Hyde, 1960).

1

2 From Figure 9, it can also be seen that the ^{230}Th tends to be associated to the phosphogypsum

3 fraction during the process. Around 87% of its input is deposited in the disposal area. The

4 remaining 13% is associated to the production of phosphoric acid, 27 % P_2O_5, and will probably

5 reach the environment via the use of phosphate fertilisers.

6

7 Quantitatively, 72.3 MBq/h of ^{230}Th are sent to the phosphogypsum piles for disposal. Almost the

8 same amount, 76 MBq/h, is associated to the phosphate rock and enters the production process.

9 Associated to the production of phosphoric acid, the ^{230}Th flux is 11.7 MBq/h, which indicates the

10 good balance established for this radionuclide during the process. The deviation is only of 10%,

11 The annual flux of ^{230}Th stored in the phosphogypsum piles due to the plant can be estimated at

12 0.85 TBq, slightly higher than the estimate for ^{238}U, due to the higher tendency of the thorium to be

13 associated to the phosphogypsum.

14

15 Finally, in Figures 10 and 11 the normalized balances for ^{226}Ra and ^{210}Pb, respectively are shown.

16 From these figures, it can first be drawn that in the case of ^{226}Ra the input and output fluxes are in

17 agreement within a deviation of 10 %, while in the case of ^{210}Pb this agreement is even better

18 (deviation between input and output fluxes of 1-2 %).

19

20 From these last two figures it is also possible to deduce that both Ra and Pb elements have a very

21 high affinity with the P phosphogypsum, which is even higher than that observed previously for

22 thorium. This conclusion can be ratified by the minor presence of both radionuclides in the

23 production phosphoric acid (27 % P_2O_5) and in the recycled phosphoric acid (22 % P_2O_5). Only 4.0

24 MBq/h in the case of ^{210}Pb and 0.30 MBq/h in the case of ^{226}Ra are associated to the production

25 phosphoric acid.

26

1 In the case of [226]Ra, the proportion of the input associated to the phosphogypsum is 99.5 %, with

2 only 0.5 % associated to the production of phosphoric acid. The behaviour of ^{210}Pb is similar to that

3 of radium. The proportion associated to the phosphogypsum being slightly lower, 93 %, with only

4 7% associated to the acid. The net fluxes stored in the disposal area can be evaluated in around 70

5 MBq/h of [226]Ra and [210]Pb.

6

7 The normalized fluxes of [232]Th, [228]Th and [228]Ra are not shown and discussed because these

8 radionuclides have similar behaviour to that observed for [230]Th and [226]Ra, respectively. This similar

9 behaviour can be explained, and is even expected, attending to the fact that the fractionation of the

10 different radionuclides in the wet acid production process are mostly due to chemical processes

11 involved being elemental and non-isotope dependent. The fact that the compared isotopes of

12 thorium and radium belong to different natural series is not relevant for their distribution and fluxes

13 during the process, mostly due to the strong acid attack of the phosphate rock in the initial reaction

14 step.

15

16 **4. Conclusions**

17 The flow and fractionation of natural radionuclides belonging to the [238]U-series have been studied

18 in detail along the wet process of a phosphoric acid production plant. Around 380 MBq/h of [238]U is

19 the intake for the five existing plants at Huelva (Spain), in secular equilibrium with their daughters,

20 associated to the raw material (sedimentary phosphate rock), being the secular equilibrium broken

21 at the initial acid digestion step.

22

23 The well known uranium enrichment in the liquid fraction (the acid) seems to be a consequence of

24 two facts: firstly, the high chemical affinity of this element for the recently produced phosphoric,

25 acid secondly, the use of additional P_2O_5 (previously enriched in uranium) in order to accelerate the

1 rock digestion. As a consequence, a fair correlation between acid P_2O_5 contents and uranium

2 concentration has been achieved.

3

4 The phosphogypsum produced during the acid attack is consequently submitted to progressive

5 washings, and the results show how the uranium concentration clearly decreases as the washing is

6 becoming more intense. This fact is probably due to the association of uranium to traces of

7 phosphoric acid remaining in the recently generated phosphogypsum. Washing and filtering

8 processes remove such traces, and for that fact uranium concentration decreases according to the

9 number of washings. On the other hand, Pb, Ra and, in some extent, Th isotopes are exclusively

10 supplied by the phosphate rock, and they remain associated to the phosphogypsum particles, being

11 subsequently stored in a disposal site located in the vicinity of the factories at a rate of around 350

12 MBq/h.

13

14 **Acknowledgements**

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13

1 **6. Figure captions.**

2

3 Figure 1. Schematic diagram of the phosphate rock milling step.

4

5 Figure 2. Schematic diagram of the phosphate rock acid attack (step 2).

6

7 Figure 3. Schematic diagram of the PHOSPHOGYPSUM filtration and washing steps (steps 3 and

8 4, respectively).

9

10 Figure 4: General configuration of the PHOSPHOGYPSUM disposal site.

11

12 Figure 5. Dependence of the ^{238}U activity concentration on the P_2O_5 concentration of the samples

13 collected in this work.

14

15 Figure 6. General scheme of the steps considered for establishing the mass/activity balances in this

16 industrial process.

17

18 Figure 7. Scheme of the P_2O_5 mass balance throughout the whole industrial process.

19

20 Figure 8. Scheme of the ^{238}U activity balance throughout the whole industrial process.

21

22 Figure 9. Scheme of the ^{230}Th activity balance throughout the whole industrial process.

23

24 Figure 10. Scheme of the ^{226}Ra activity balance throughout the whole industrial process.

25

26 Figure 11. Scheme of the ^{210}Pb activity balance throughout the whole industrial process.

1

Code	Description
Step 1: MILLING AND GRINDING	
M-1	Phosphate rock before milling and grinding. It was taken from the silos where it is stored after its reception in the factory
M-2	Phosphate rock collected just after its grinding in the ball mill and before its transportation by an ascendant current air to several cyclones
M-3	Grinded phosphate rock collected just before its entrance in the digester
Step 2: ACID ATTACK	
A-1	22% P_2O_5 coming from the filtration step and used to favour the digestion.
A-2	Grinded phosphate rock feeding the digester.
A-3	Pulp formed in the digester, and collected from the compartment 5
A-4	Pulp collected from compartment 7 of the digester, just after passing from the flash-cooler
A-5	Pulp collected in the compartment 6 of the digester, just before to be transported to the filtration step
A-6	Water from Deposit B collected before its transportation to the filtration step
A-7	Water returning to the factory from the ponds used for the storage of PG
A-8	Fresh waters supplied from outside the process .
A-9	Water collected in deposit A, used to dilute the 98 % sulphuric acid.
Step 3: FILTERING AND WASHING	
F-1 = A-5	Pulp collected just after leaving compartment 6 of the digester and before to be suctioned and washed
F-2	27 % P_2O_5 extracted from the pulp coming from the digesters by suction.
F-3	PG collected before to be washed, and after the extraction of the 27% P_2O_5
F-4 = A-1	22 % P_2O_5 extracted from the PG in the first washing and used to favour the reaction in the digesters.
F-5	12 % P_2O_5 extracted from the PG in the second washing and used for the performance of the first washing
F-6	PG collected after the first washing with 12 % P_2O_5
F-7	5 % phosphoric acid extracted from the PG in the third washing and used for the performance of the second washing
F-8	PG collected after the second washing with 5 % P_2O_5
F-9	Water from Deposit C, used for the third washing of the PG
F-10	Waste water collected from different parts of the plan to deposit B and used for the washing of the filter clothes
F-11	"Fresh PG" collected after third washing just before to be transported to deposit D
F-12	Residual waters coming from a plant of the factory devoted to the production of SA from pyrites and used to form the solution with the PG in suspension to be transported into the PG stacks.
F-13	Suspension of PG plus water which is pumped into the storage area
F-14	Mud formed at the bottom of the tank where the 27 % P_2O_5 is stored
F-15	Floating material at the upper of the tank where the 27 % P_2O_5 is stored
Step 4: CONCENTRATION	
C-1	Phosphoric acid at 54% P_2O_5 obtained after the concentration process
C-2	Phosphoric acid (32 % P_2O_5) which is feeding to the condenser after flocculation

2
3   Table 1: Codes and description of samples taken along the whole industrial process.

Sample Code	Sample Type	238U	234U	230Th	226Ra	210Pb	232Th	228Th	228Ra
M1	Phosphate Rock	1650 ± 90	1650 ± 90	1670 ± 70	1610 ± 80	1660 ± 90	25 ± 2	21 ± 2	22 ± 2
M2		1650 ± 90	1650 ± 90	1490 ± 60	1630 ± 80	1600 ± 90	24 ± 2	20 ± 2	19 ± 2
M3		1630 ± 90	1640 ± 90	1570 ± 70	1640 ± 80	1610 ± 100	22 ± 1	23 ± 2	21 ± 2
A2		1680 ± 100	1680 ± 10	1670 ± 80	1380 ± 70	1440 ± 100	33 ± 4	17 ± 1	20 ± 1
A1	22% P$_2$O$_5$	870 ± 50	870 ± 50	95 ± 4	3.0 ± 0.4	74 ± 14	53 ± 11	1.7 ± 0.4	< 1.8
A3L	Cake Dig. Liquid Fraction	1000 ± 70	980 ± 70	245 ± 22	5.5 ± 0.5	76 ± 12	3.0 ± 0.6	3.8 ± 0.5	< 1.9
A4L		1300 ± 90	1280 ± 90	246 ± 19	6.7 ± 0.5	82 ± 13	3.2 ± 0.6	8.0 ± 0.7	6.7 ± 0.5
A5L		1340 ± 90	1330 ± 90	425 ± 78	4.0 ± 0.4	60 ± 12	6.5 ± 1.4	4.0 ± 0.5	< 1.0
A3S	Cake Dig. Solid Fraction	460 ± 30	460 ± 30	510 ± 50	470 ± 20	520 ± 100	14 ± 2	9.4 ± 0.8	14 ± 1
A4S		560 ± 40	560 ± 40	690 ± 30	760 ± 40	870 ± 160	14 ± 2	14 ± 1	14 ± 2
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
A7		182 ± 17	183 ± 17	N.M.	< 0.6	8 ± 5	N.M.	< 1.6	< 1.2
A8		0.054 ± 0.004	0.051 ± 0.004	N.M.	< 0.9	< 11	N.M.	< 1.5	< 0.9
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

Table 2: Activity concentrations (Bq/kg) obtained for the samples collected along the milling and digestion steps. "L" = Liquid fraction; "S" = Solid fraction. "N.M.": Not measured.

Sample Code	Sample Type	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{232}Th	^{228}Th	^{228}Ra
F1L =A5L	Pulp	1340 ± 90	1330 ± 90	425 ± 78	4.0 ± 0.4	60 ± 12	6.5 ± 1.4	4.0 ± 0.5	< 1.0
F1S = A5S	Cake	450 ± 30	450 ± 30	750 ± 30	590 ± 25	590 ± 120	16 ± 2	11 ± 2	9.4 ± 1.1
F2	27% P$_2$O$_5$	1070 ± 110	1090 ± 110	230 ± 30	5.6 ± 0.5	78 ± 15	9.8 ± 1.8	3.9 ± 0.5	< 1.8
F4 = A1	22% P$_2$O$_5$	870 ± 50	870 ± 50	95 ± 4	3.0 ± 0.4	74 ± 14	53 ± 11	1.7 ± 0.4	< 1.8
F5	12% P$_2$O$_5$	470 ± 40	470 ± 40	80 ± 10	6.1 ± 0.5	< 225	6.0 ± 1.5	< 1.7	< 1.9
F7	5% P$_2$O$_5$	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
F13L	Gypsum	280 ± 20	280 ± 20	1.1 ± 0.10	9.1 ± 0.3	6 ± 5	0.05 ± 0.02	< 1.5	< 1.8
F13S	+ water	250 ± 20	260 ± 20	700 ± 30	525 ± 30	610 ± 80	21.6 ± 2.4	< 3	8.9 ± 1.3
F9	waters	230 ± 20	230 ± 20	N.M.	0.33 ± 0.30	< 16	12.3 ± 1.0	< 1.6	< 1.2
F10	waters	56 ± 5	56 ± 5	0.31 ± 0.03	2.6 ± 0.4	< 15	0.11 ± 0.02	< 1.5	< 1.9
F12	waters	0.26 ± 0.02	0.28 ± 0.02	0.74 ± 0.02	< 0.8	< 9	0.029 ± 0.003	< 1.0	< 1.2
F14L	Sludges	2090 ± 170	2100 ± 170	1250 ± 150	7.4 ± 0.5	46 ± 10	22 ± 3	16.3 ± 1.2	1.7 ± 0.5
F15L	Sludges	1260 ± 80	1240 ± 80	250 ± 30	4.5 ± 0.4	84 ± 15	5.2 ± 1.1	6.0 ± 0.6	< 1.7
F14S	Sludges	1230 ± 70	1230 ± 70	2000 ± 150	4300 ± 220	1900 ± 90	28 ± 6	32 ± 3	65 ± 6
F15S	Sludges	910 ± 60	900 ± 55	910 ± 25	1310 ± 70	1420 ± 160	12.9 ± 1.0	10.4 ± 1.2	17.8 ± 1.9
C1	32% P$_2$O$_5$	1300 ± 70	1320 ± 70	N.M.	3.6 ± 0.3	< 135	N.M.	6.5 ± 0.4	< 0.9
C2	54% P$_2$O$_5$	1830 ± 180	1810 ± 180	N.M.	7.9 ± 0.5	109 ± 14	N.M.	13.2 ± 1.4	< 1.0

Table 3: Activity concentrations (Bq/kg) obtained for the samples collected along the filtration, washing and acid concentration steps. "L" = Liquid fraction; "S" = Solid fraction. "N.M.": Not measured.

Sample Code	Sample Type	$^{234}U/^{238}U$	$^{230}Th/^{238}U$	$^{226}Ra/^{238}U$	$^{210}Pb/^{238}U$	$^{226}Ra/^{230}Th$	$^{210}Pb/^{226}Ra$	$^{232}Th/^{238}U$ ($\times 10^2$)
M3	Phosphate rock	1.01 ± 0.08	0.96 ± 0.07	1.01 ± 0.07	0.99 ± 0.08	1.04 ± 0.07	0.98 ± 0.08	1.4 ± 0.1
A4L	Cake digester	0.98 ± 0.10	0.19 ± 0.02	0.005 ± 0.001	0.06 ± 0.01	0.027 ± 0.003	12 ± 2	0.25 ± 0.05
A4S		1.00 ± 0.10	1.23 ± 0.11	1.36 ± 0.12	1.61 ± 0.32	1.10 ± 0.08	1.14 ± 0.22	2.5 ± 0.4
A6	Water ponds	1.00 ± 0.09	< 0.0005	0.020 ± 0.002	0.44 ± 0.09	> 40	22 ± 5	0.27 ± 0.02
A7		1.01 ± 0.13	N.M.	0.007 ± 0.016	0.04 ± 0.03	N.M.	67 ± 172	-
F2	27% P_2O_5	1.02 ± 0.15	0.21 ± 0.03	0.0052 ± 0.0007	0.073 ± 0.016	0.024 ± 0.004	14 ± 3	0.9 ± 0.2
F5	12% P_2O_5	1.00 ± 0.11	0.17 ± 0.03	0.013 ± 0.002	< 0.48	0.076 ± 0.012	< 75	1.3 ± 0.3
F8	Gypsum	1.08 ± 0.10	1.98 ± 0.18	1.80 ± 0.15	1.72 ± 0.21	0.91 ± 0.07	0.96 ± 0.11	9 ± 1
F13S		1.04 ± 0.10	2.84 ± 0.23	2.11 ± 0.17	2.46 ± 0.34	0.74 ± 0.05	1.17 ± 0.16	9 ± 1
F14L	Sludges	1.00 ± 0.11	0.59 ± 0.09	0.0035 ± 0.0004	0.022 ± 0.005	0.0060 ± 0.0008	6.2 ± 1.4	1.1 ± 0.2
F14S		1.00 ± 0.08	1.62 ± 0.15	3.5 ± 0.3	1.54 ± 0.11	2.16 ± 0.20	0.44 ± 0.03	2.3 ± 0.5
C2	54% P_2O_5	0.99 ± 0.14	N.M.	0.0043 ± 0.0005	0.059 ± 0.010	N.M.	13.8 ± 2.0	-

Table 4: Activity ratios obtained for the most representative samples collected along the whole industrial process. "L" = Liquid fraction; "S" = Solid fraction. "N.M.": Not measured.

1
2

Sample code	^{238}U, ^{234}U	^{226}Ra	^{228}Th	^{228}Ra
AG1	223 ± 18	< 0.69	1.6 ± 0.3	< 1.4
AG2	219 ± 22	< 0.86	5.3 ± 0.6	< 1.0
AG3	204 ± 22	< 0.87	< 1.6	< 1.6
AG4	215 ± 21	< 0.83	1.7 ± 0.4	<1.6
AG5	214 ± 21	< 0.90	8.2 ± 0.7	< 1.6
AG6	217 ± 21	< 0.89	6.5 ± 0.6	< 1.6

3
4 Table 5: Obtained activity concentrations (Bq/kg) for the PG transportation water samples collected
5 in this work measured by gamma spectrometry.
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1   Fig. 1

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1   Fig. 2

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1   Fig. 3

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1   Fig. 4

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1   Fig. 5

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The figure shows a plot of ^{238}U activity concentration (Bq/kg) versus P_2O_5 contents (%). The fitted equation is:

$$a(^{238}U) = (108 \pm 25) + (35 \pm 2)[P_2O_5]$$

$$R^2 = 0.9860$$

Data points are labelled F7, F5, F4, F2, C1, and C2.

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1   Fig. 6

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1   Fig. 7

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1   Fig. 8

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1   Fig. 9

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1 Fig. 10

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1   Fig. 11

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