Fluxes of ^{238}U decay series radionuclides in a dicalcium phosphate industrial plant

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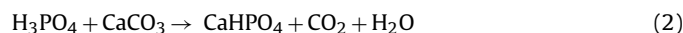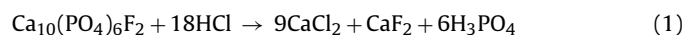
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ABSTRACT

The production of dicalcium phosphate (DCP) is part of the phosphate industry, which has been recently included in the positive list of the NORM industries defined in the revised version of the EU-BSS (Euratom 29/96). The objective of the present work is to study specific concentrations and fluxes of ^{238,234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po at the different stages of the DCP production. Results showed highest activities of ^{238}U and ^{210}Pb were found in DCP (1500–2000 Bq kg^{-1}); ^{230}Th and ^{210}Po were released together with the sludges (1600–2000 Bq kg^{-1}) and ^{226}Ra presented particularly high activities in water (48×10^3 Bq m^{-3}) and in the reactor scales (115×10^3 Bq kg^{-1}). Fluxes of radionuclides showed that ^{238}U outflows were equally distributed between sludges (16×10^3 kBq h^{-1}) and dicalcium phosphate (20×10^3 kBq h^{-1}); ^{230}Th and ^{210}Po were almost entirely released in the sludges (30×10^3 kBq h^{-1}) and the greatest ^{210}Pb outflow was the DCP current (25×10^3 kBq h^{-1}). ^{226}Ra was mainly discharged through the water effluent (12×10^3 kBq h^{-1}). This work highlights the importance of studying the industrial processes involving NORM, as minor changes in the production steps lead to different radionuclide distribution in the process.

1. Introduction

Calcium and phosphorous are essential elements for the health, growth and reproductivity of animals, but the levels of these elements provided by normal pasture and plant material are not sufficient for farm animals [1]. Therefore, an additional and adequate supply of calcium and phosphorous is required if optimal livestock health and productivity are to be achieved. Most inorganic phosphates used for this purpose are derived from natural phosphate rocks [2]. However, all the natural calcium and phosphorous deposits, although being worldwide abundantly available, contain fluorides in toxic quantities, which cannot be tolerated in long-term feeding animals. More to this point, inorganic phosphates in their natural form cannot be metabolized by animals [1,2]. Therefore, a chemical or thermal treating of the natural ores is required to remove the fluorides, raise the mineral concentration and enhance its biological availability [1]. A widely used product of the phosphate rock treatment is dicalcium phosphate (DCP). This phosphate-based product is used as a feed supplement for domestic animals, containing the optimum amounts of calcium (~21%) and phosphorous (~18%) for the animal growth.

Inorganic feed phosphates (i.e. monocalcium phosphate, dicalcium phosphate, etc.) are mainly produced by digesting the phosphate rock with sulphuric acid and reacting the resulting purified feed-grade phosphoric acid with a calcium, magnesium, sodium or ammonium source or a mixture of them. Another way to produce inorganic feed phosphates is by treating the phosphate rock with hydrochloric acid, leading to crystalline dicalcium phosphate by the reactions below [2]:

$$Ca_{10}(PO_4)_6F_2 + 18HCl \rightarrow 9CaCl_2 + CaF_2 + 6H_3PO_4 \quad (1)$$

$$H_3PO_4 + CaCO_3 \rightarrow CaHPO_4 + CO_2 + H_2O \quad (2)$$

An inconvenient associated to the use of sedimentary phosphate rocks is the high contents of ^{238}U (Fig. 1), with typical activities of 1500–1700 Bq kg^{-1}, which is generally in secular equilibrium with its decay products [3]. The mining and processing of the phosphate ores leads to the redistribution of ^{238}U and its decay chain products among the various products, by-products and wastes of the phosphate industry. The chemical behavior and distribution of radionuclides has been studied in the phosphate industry dedicated to the production of fertilizers. In that case, both the final product and the by-product (i.e. phosphogypsum) may contain significant amounts of ^{226}Ra, as well as other radionuclides of the ^{238}U decay series, which may be of radiological concern [4,5]. Regarding the specific case of DCP production, a previous study showed that several radionuclides of the ^{238}U decay series accumulate differently in the final product depending on the acid used for the

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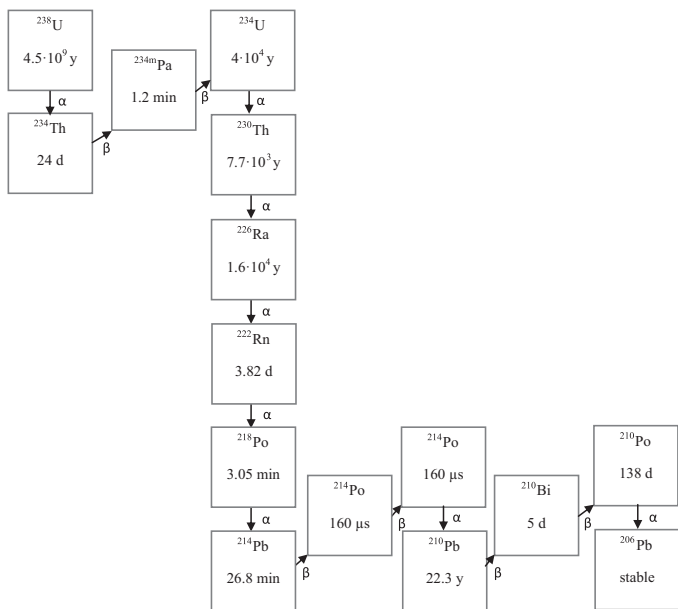E-mail address: Nuria.Casacuberta@uab.es (N. Casacuberta).

Fig. 1. Diagram of the ^{238}U decay series, indicating the half-life of each nuclide.

phosphate rock digestion: whereas the rock digestion with sulphuric acid leads to high activity concentrations of ^{238,234}U and ^{230}Th in DCP, the hydrochloric digestion of the raw material results in high accumulation of ^{238,234}U, ^{210}Pb and ^{210}Po in the final product [6]. Nevertheless, and to our best knowledge, only one study on the fluxes of radionuclides during the production of DCP produced via hydrochloric acid has been published [7], at an industrial plant that slightly differs from the industrial process presented herein.

The Basic Safety Standards Directive for protection against ionizing radiation and for the safety of radiation sources [8] has been recently revised by the regulatory authorities, resulting in a new Euratom Basic Safety Standards Directive, which is still under the form of a draft [9]. This new Directive shall include a positive list of NORM industries and obliges the Member States to identify the practices involving Naturally Occurring Radioactive Materials, its activities for the ^{238}U series being limited to 1 Bq g^{-1} (or 1000 Bq kg^{-1}). As this might be the case for DCP production, the objective of this work is to study the radionuclide activities in the resulting products and by-products in a DCP industry in South Europe. Fluxes of radionuclides in the whole process have also been analyzed in order to evaluate the radionuclide distribution in the particular case of the hydrochloric acid digestion of the phosphate rock. The study focuses on the ^{238}U decay series (i.e. ^{238,234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po), since these are the radionuclides found in a greater proportion in phosphate rocks from sedimentary origin [3].

2. Materials and methods

2.1. Production of dicalcium phosphate (DCP)

Several samples were collected at different stages of the DCP production process (Fig. 2). This process is described below and sample codes are indicated in capital letters.

2.1.1. Phosphate rock digestion

In the DCP production process, phosphate rock (PR) from Morocco ores is digested with hydrochloric acid and the digested pulp (PRAD) is settled in a decanter tank (decanter tank 1). The production line is herein divided in two main streams: the sludges line and the DCP production line.

2.1.2. Sludge line

The decanted solid fraction containing CaF$_2$ corresponds to the non digested fraction of the phosphate rock (NDPR) and is brought to a re-digestion tank. The product of this digestion is decanted in tank 2, where the liquid fraction is recirculated to the re-digester tank, and the solid fraction is released as sludge (SG-DCP). This sludge is finally filtered together with wastes coming from a neighboring industrial plant. The liquid fraction is driven to the water treatment plant where it gathers together with the water effluent coming from the decanter tank 3 (i.e. WT-DCP effluent), whereas the solid fraction is released as general sludge (SG-GN) together with the solid fraction coming from the water treatment plant and other wastes from the neighboring plants.

2.1.3. DCP production line

The digested fraction of the phosphate rock (DPR) is brought to the precipitation tanks where CaCO$_3$ is added in order to precipitate the P$_2$O$_5$ from the phosphate solution. A white pulp is obtained (DCPCR), being firstly transported to a washer and finally to a filter where the liquid fraction is removed from the un-filtered fraction. The liquid fraction is released to the decanter tank 3, where the decanted fraction is recirculated to the decanter tank 1 and the supernatant (WT-DCP) is driven to the water treatment plant. The decanted fraction (white sludges) corresponds to one of the major recirculating flows (RE) of the production process. This white sludge is released in the decanter tank 1, where the pH is adjusted and helps on the precipitation of CaF$_2$, thus following the sludge line above described. The supernatant of the tank 3 (WT-DCP) is brought to the water treatment plant. After treatment, the solid fraction is released together with the SG-GN, whereas the water effluent is released to the river (WT-GN). The end-product of this process is the DCP, which is obtained after drying the un-filtered fraction from the DCP filters.

The samples described above and summarized in Table 1 were collected at three different times: May 2007, November 2007 and April 2008. The results presented here correspond to one, two or three results obtained in the sampling series. Additional information about the mass, P$_2$O$_5$, CaF$_2$ and CaCl$_2$ fluxes (kg h^{-1}) is also included in Table 1.

Samples of the precipitates formed within the digester were also collected in April 2010. These scales codified as SC-1 to SC-8 were sampled at the upper part of the digester (SC-1 to SC-3), in the middle walls (SC-7 and SC-8), in the output pipe (SC-4) and in the DCP precipitation tanks (SC-5) where white scales are formed.

2.2. Sample pre-treatment and analysis of radionuclide contents

Solid samples were dried at 80 °C and homogenized before their analysis. For the quantification of uranium and thorium isotopes, between 100 and 300 mg of sample was digested using a mixture of HCl, HNO$_3$ and H$_2$O, after addition of known amounts of internal tracers (^{229}Th, ^{232}U). For the radiochemical separation of U and Th, the method described in Horwitz et al. [10] was used, based in extraction chromatography using UTEVA resins. Samples were loaded in a 3 M HNO$_3$ media, Th is eluted with 25 mL of 5 M HCl, 0.05 M oxalic acid and U was stripped with 15 mL of 0.01 M HCl. U and Th isotopes were electrodeposited on 2.2 cm diameter silver discs in plastic cells using platinum wire as anode [11].

For the quantification of ^{210}Pb and ^{210}Po in solid samples, between 100 and 300 mg of sample was digested with a mixture of HCl, HNO$_3$ and HF as described in Sanchez-Cabeza et al. [12] using ^{209}Po as internal yield tracer. Once digested, the solution was evaporated to dryness and made 1 M HCl. Polonium isotopes were auto-plated onto 2.2 cm silver discs for 6–7 h at 70 °C with constant stirring. Solutions obtained from the analysis of ^{210}Po were stored for 1.5 years to determine ^{210}Pb through the measurement of
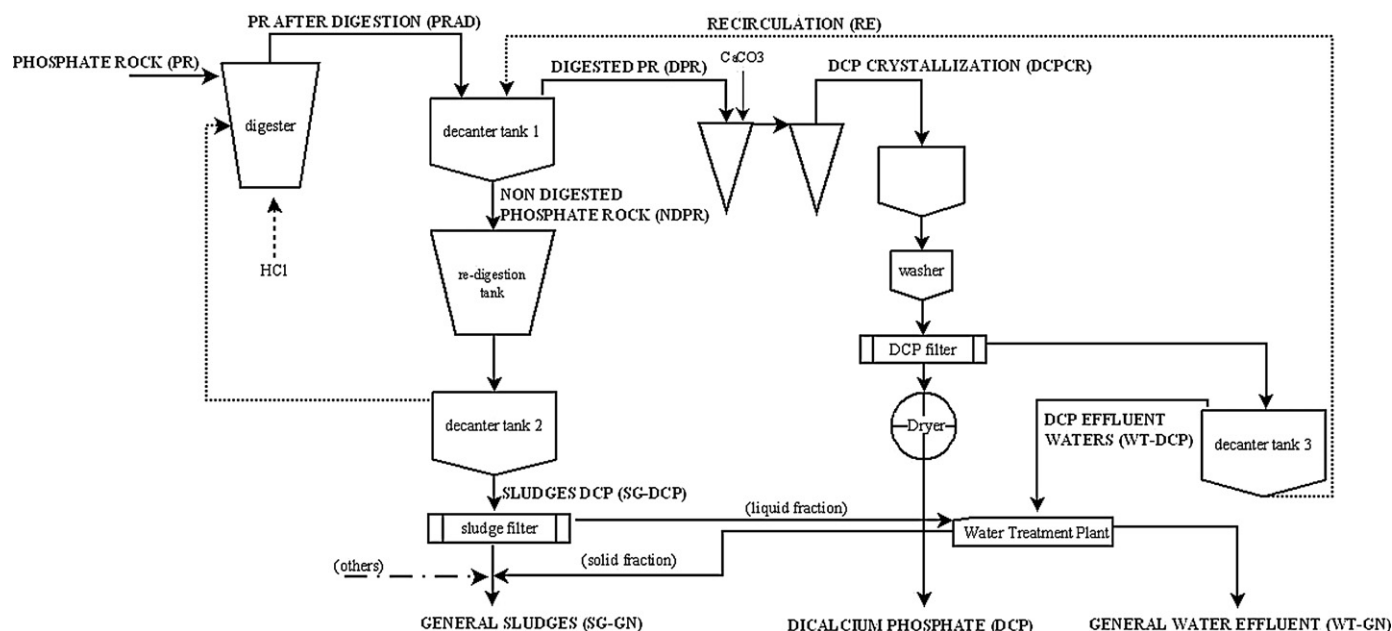
Fig. 2. Diagram of the DCP production process. Samples analyzed are indicated in capital letters (acronyms in parenthesis). See text for details.

its grown granddaughter ^{210}Po. Appropriate decay and in-growth corrections were applied to determine the concentrations of both ^{210}Pb and ^{210}Po at sampling time.

Liquid samples were filtered through 1 μm filters (Whatman Millipore) and acidified with HCl to pH ~1 and spiked with known amounts of ^{209}Po. Pre-concentration of ^{210}Pb and ^{210}Po in water samples was carried out by iron hydroxide precipitation in a basic media. The Fe(OH)$_3$ precipitates were centrifuged in a sealed tube and redissolved with concentrated HCl. Auto-plating of polonium isotopes and quantification of both ^{210}Po and ^{210}Pb at time of sampling was carried out as described above.

Alpha emitters activities (i.e. U, Th and Po isotopes) were obtained by alpha-particle spectrometry using Passivated Implanted Planar Silicon (PIPS) detectors.

^{226}Ra was analyzed by gamma spectrometry through the main line emission of its daughter nuclide ^{214}Pb (351 keV). Between 80 and 100 g of solid samples were placed into 100 cm^3 geometries, which were sealed and stored for 3 weeks to ensure secular equilibrium between ^{226}Ra and its short-lived daughters. Liquid samples were pre-concentrated from 4–5 L to 0.5 L by evaporation and placed in a Marinelli geometry, sealed and stored the same way as solid samples. Geometries were measured for 1–3 days in a coaxial HPGe detector (GMX, EG&G Ortec). Analyses of the spectra were carried out using the Genie 2000 software.

3. Results and discussion

Results on the specific activities of the ^{238}U decay series radionuclides (i.e. ^{238,234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po) in each of the analyzed samples are shown in Fig. 3. The data includes both the dissolved and the particulate fractions. It is observed that, in general, specific concentrations of all radionuclides in the phosphate rock (PR) were in secular equilibrium between them and agree well with those reported for phosphate rocks of Morocco ores [13]. However, the secular equilibrium of the isotopes of the ^{238}U decay series in phosphate ores was subject to disruption when digesting the phosphate rock with hydrochloric acid: all other samples presented a non homogeneous distribution of the activities. A specific study of the fluxes of each radionuclide was performed in order to understand the chemical pathway of each radionuclide in the described industrial production process of dicalcium phosphate (Table 2). Fluxes (expressed in kBq h^{-1}) were calculated by multiplying the specific activities of each radionuclide in each sample by the mass flux at each step of the production process (kg h^{-1}). Ratios of the output to input fluxes were calculated (OIR) to validate the balances, and main outflows are summarized in Fig. 4. A detailed discussion is done below for each of the six different radionuclides analyzed (i.e. ^{238,234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po).

Table 1

Description of samples collected at different stages of the DCP production process and the scales formed at the digesters. Information on the mass, P$_2$O$_5$, CaF$_2$ and CaCl$_2$ fluxes was provided by the company, and is presented re-scaled.

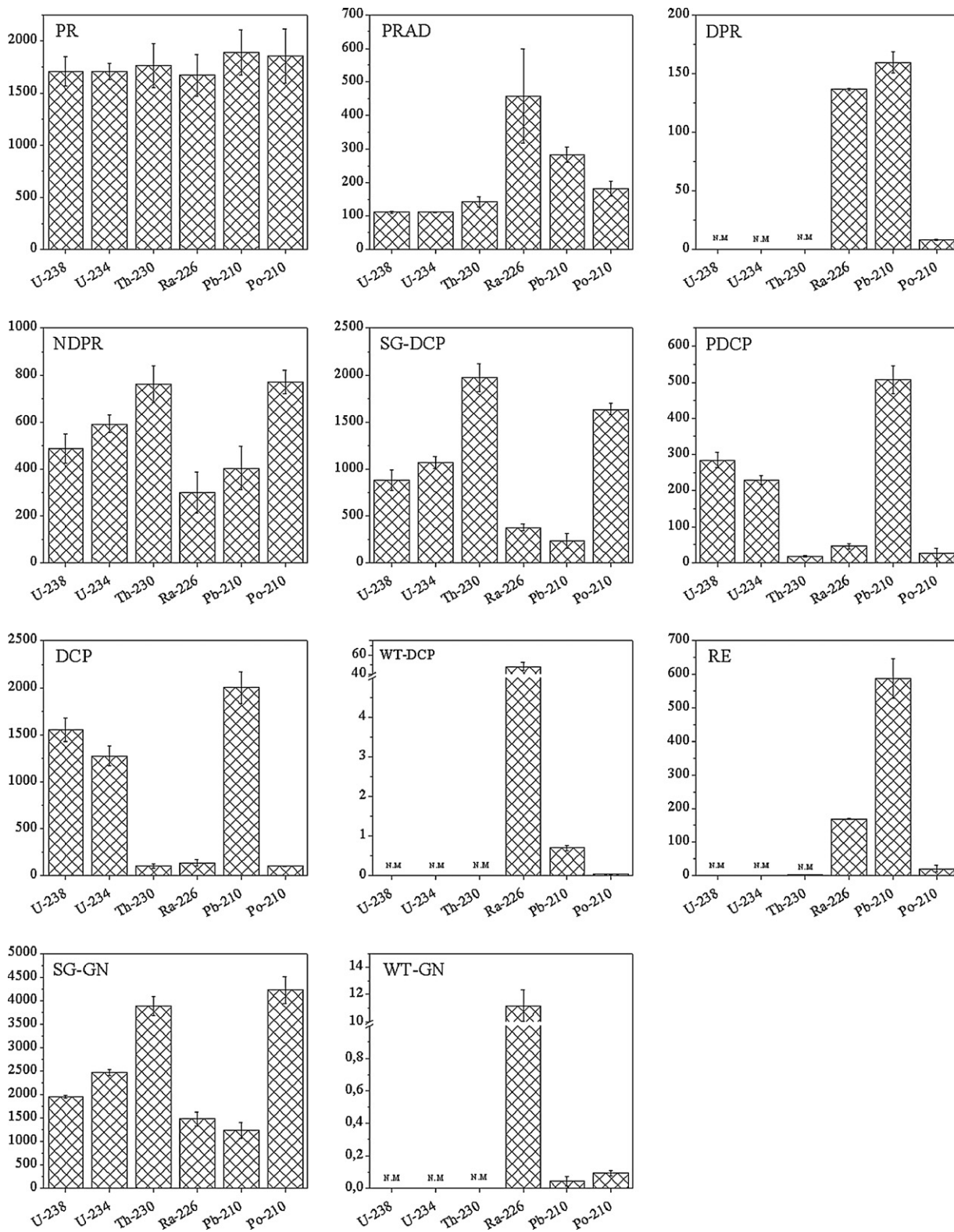|	Sample description	Mass flux (kg h^{-1}) × x	P$_2$O$_5$ flux (kg h^{-1}) × x	CaF$_2$ flux (kg h^{-1}) × x	CaCl$_2$ flux (kg h^{-1}) × x
PR	Phosphate rock	2	213	7790	
PRAD	Phosphate rock after digestion	20	275	7647	76
DPR	Digested phosphate rock	21	222	312	69
NDPR	Non digested phosphate rock	4	71	7334	11
SG-DCP	Sludges exclusive from DCP production	2	11	7254	3
PDCP	Precipitation of DCP after Ca(OH)$_2$ and CaCO$_3$	8	213	317	23
DCP	Dicalcium phosphate	2	201	301	1
WT-DCP	Water coming from the DCP production line	31	1	13	55
RE	Recirculation	3	19	1	4
SG-GN	General sludges of the industry plant	1			
WT-GN	General waters after treatment	37			

Fig. 3. Specific concentrations of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po (Bq kg^{-1}) in different samples collected during the production process of dicalcium phosphate.

3.1. Uranium

Initial specific concentrations of ^{238}U and ^{234}U in the phosphate rock (PR) were 1709 ± 138 Bq kg^{-1}, which are diluted to 111 ± 4 Bq kg^{-1} and 142 ± 8 Bq kg^{-1} for ^{238}U and ^{234}U, respectively, just after digestion of the raw material (PRAD). Concentrations

of ^{238}U in the sludge line were 486 ± 31 and 880 ± 55 Bq kg^{-1} in the non-digested fraction of the PR (NDPR) and the sludges (SG-DCP), respectively. ^{234}U presented slightly higher concentrations; 592 ± 37 and 1065 ± 63 Bq kg^{-1} in NDPR and SG-DCP, respectively. For both uranium isotopes, the highest activities were found in the end-product (DCP) and in the general sludges (SG-GN): 1553 ± 123

Table 2
Radionuclide fluxes at different stages of the DCP production process. Description of each sample is provided in Table 1. Input fluxes correspond to the PR flow; output fluxes are the sum of sludges (SG-DCP), water (WT-DCP) and dicalcium phosphate (DCP).

Sample	^{238}U (kBq h^{-1})	^{234}U (kBq h^{-1})	^{230}Th (kBq h^{-1})	^{226}Ra (kBq h^{-1})	^{210}Pb (kBq h^{-1})	^{210}Po (kBq h^{-1})
PR	30780 ± 2489	30787 ± 1429	31759 ± 3766	30067 ± 3588	34057 ± 3892	33417 ± 4729
PRAD	17639 ± 289	17639 ± 291	22517 ± 1213	28286 ± 278	45030 ± 1752	28993 ± 1753
DPR	N.M	N.M	N.M	22470 ± 71	26256 ± 743	1344 ± 58
NDPR	15892 ± 1001	19330 ± 1201	24874 ± 1294	9784 ± 2868	13187 ± 2993	25204 ± 816
SG-DCP	15648 ± 984	18950 ± 1128	35126 ± 1326	6692 ± 623	4127 ± 1421	29063 ± 559
PDCP	18683 ± 698	15009 ± 782	1211 ± 82	3015 ± 460	33291 ± 2495	1719 ± 481
DCP	19772 ± 1566	16207 ± 1357	1270 ± 164	1750 ± 423	25506 ± 2156	1279 ± 51
WT-DCP	N.M	N.M	N.M	11391 ± 1044	167 ± 9	9 ± 1
RE	17 ± 1	15 ± 1	29 ± 4	3319 ± 11	11534 ± 571	399 ± 96
SG-GN	15260 ± 148	19290 ± 454	30372 ± 805	11533 ± 1183	9661 ± 1313	33022 ± 1131
WT-GN	N.M	N.M	N.M	3258 ± 337	13 ± 4	27 ± 2
Inputs	30780 ± 2489	30787 ± 1429	31759 ± 3766	30067 ± 3588	34057 ± 3892	33417 ± 4729
Outputs	35420 ± 1849	35157 ± 1765	36396 ± 1336	19833 ± 1287	29799 ± 2582	30351 ± 561
OIR	1.15 ± 0.11	1.14 ± 0.08	1.15 ± 0.14	0.66 ± 0.09	0.87 ± 0.13	0.91 ± 0.13

and 1952 ± 19 Bq kg^{-1}, respectively for ^{238}U, and 1273 ± 107 and 2467 ± 58 Bq kg^{-1}, respectively for ^{234}U.

In terms of ^{238,234}U fluxes, it was observed that the input flow $(31 \times 10^3$ kBq h$^{-1})$ was equally split (Fig. 4) between the sludges and the DCP production lines $((16–19) \times 10^3$ and $(16–20) \times 10^3$ kBq h^{-1}, respectively). The output to input fluxes ratio (OIR) was 1.15 ± 0.11 for ^{238}U and 1.14 ± 0.08 for ^{234}U, thus giving a fairly accurate picture of the flow of uranium radionuclides in the process.

These results slightly differ from those obtained in Gäfvert et al. [7], where about 75% of the total activity inflow was retained in the DCP. The difference might relay on the digestion of the raw material, which the industrial process studied here is performed in two steps instead of one. Disparity in the distribution of uranium is observed in other industrial plants where the phosphate rock is digested with sulphuric acid for the production of phosphoric acid: Bolívar et al. [14] observed that the uranium flow was equally divided between the phosphoric acid flow and the phosphogypsum, while other studies concluded that a larger proportion of the uranium inputs (~80%) is separated into the acid stream [15,16]. Indeed, the distribution of uranium isotopes during the acid digestion of the rock may be controlled by a number of factors, such as redox potential, digestion temperature and coprecipitation with fluorides [17,18].

3.2. Thorium

As for the case of uranium, the initial specific activities of ^{230}Th in the phosphate rock (PR) (1763 ± 209 Bq kg^{-1}) were heterogeneously distributed in the different products and by-products, after digestion of the raw material with hydrochloric acid. The flow containing the digested rock (PRAD) presented about 8% of the initial concentration (142 ± 8 Bq kg^{-1}), that increased along the sludge line. The concentration of ^{230}Th in the non-digested fraction of the rock (NDPR) was of 761 ± 40 Bq kg^{-1}, and even higher in the sludge (SG-DCP), of 1975 ± 75 Bq kg^{-1}. The highest specific activity was observed in the general sludge (SG-GN), with 3885 ± 103 Bq kg^{-1}. The DCP production flow presented low ^{230}Th activities: the end-product (DCP) had 100 ± 13 Bq kg^{-1}.

In terms of the ^{230}Th fluxes, a large fraction of the input fluxes was released in the sludges $(35 \times 10^3$ kBq h$^{-1})$, and only about 4% in the final product (Fig. 4). Thorium follows the CaF$_2$ pathway (see Table 1), as it may be complexed by fluoride ions to form ThF$_4$, which coprecipitates with CaF$_2$. As for the case of uranium, a good mass balance was obtained for the ^{230}Th fluxes, since the OIR did not significantly deviate from unity (1.15 ± 0.14).

The distribution of ^{230}Th in the production process here studied agrees well with the results reported by Gäfvert et al. [7], where

only about 1% of the total ^{230}Th was found in DCP and the rest was held in sludges. When the phosphate rock is digested with sulphuric acid, the enrichment factors for ^{230}Th from phosphate rock to wastes (i.e. phosphogypsum) are of 80% [4,14]. Therefore, regardless of the acid used for the rock digestion, Th is likely bound to and transported with extremely fine-grained particulates rather than being present as dissolved species in the acid flow [17].

3.3. Radium

The specific concentrations of ^{226}Ra in the various industrial stages were more evenly distributed than those of uranium and thorium. The initial concentration in the phosphate rock (PR) was 1669 ± 199 Bq kg^{-1}, which after digestion (PRAD) was diluted to 178 ± 2 Bq kg^{-1}. Specific concentration following the sludge line was 299 ± 88 Bq kg^{-1} in the non-digested fraction of the phosphate rock (NDPR) and 376 ± 35 Bq kg^{-1} in the sludge (SG-DCP). The DCP production line had lower specific concentration, leading to an end-product (DCP) with 137 ± 33 Bq kg^{-1}. ^{226}Ra concentrations were notably high both in the water flux (WT-DCP), with 48 ± 4 Bq L^{-1}, and in the recirculation flow (RE), with 169 ± 1 Bq kg^{-1}. It is also to note the increase of ^{226}Ra concentrations in the general sludges (SG-GN) (1475 ± 151 Bq kg^{-1}) compared to the DCP sludge (376 ± 35 Bq kg^{-1}), accompanied by the decrease of the concentration in the general waters WT-GN (11 ± 1 Bq L^{-1}) compared to the waters coming from the decanter tank 3 (WT-DCP). The water treat-
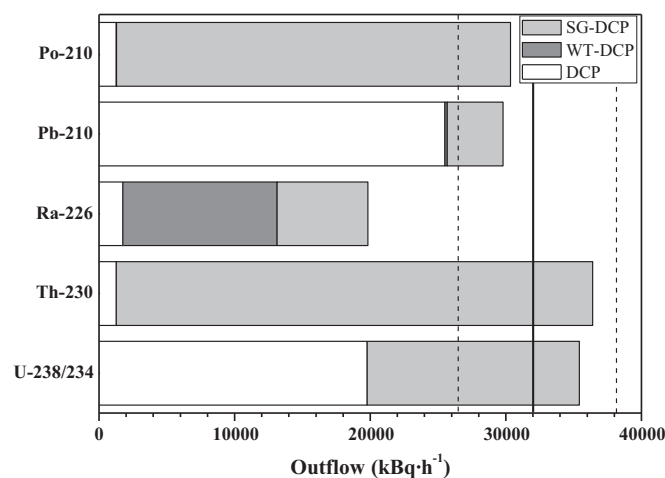

Fig. 4. Outflow distribution of each radionuclide in the sludges (SG-DCP), the water effluent (WT-DCP) and the dicalcium phosphate (DCP). The vertical solid line represents the average inflow and the dashed lines the minimum and maximum inflows.
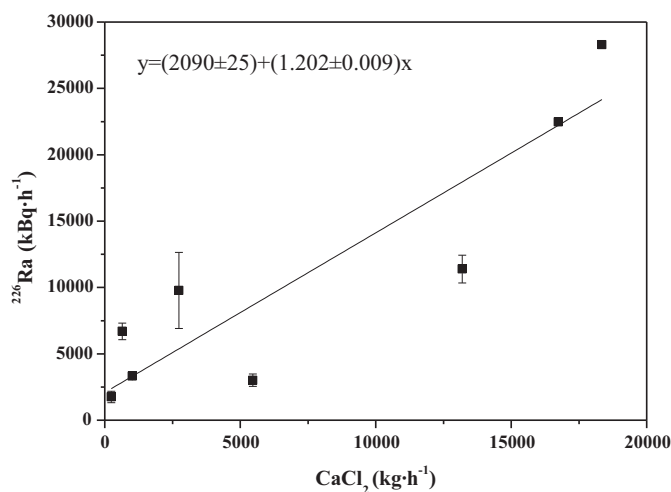
Fig. 5. $CaCl_2$ fluxes versus ^{226}Ra fluxes at each stage of the DCP production process. $R^2 = 0.98$ and $p < 0.001$.

Fig. 6. ^{226}Ra concentration in the digester scales samples analyzed at different stages of the DCP production process. SC-1, SC-2 and SC-3 correspond to the upper wall of the digester; SC-4 represents the scales found in the common output pipe of the digesters; SC-5 is the white scales in the precipitation tanks; SC-7 and SC-8 are the scales found in the digester tank walls.

ment plant is therefore efficient in reducing the concentrations of ^{226}Ra and ^{210}Pb in water.

Regarding ^{226}Ra fluxes, about one third of the total input $(30 \times 10^3 \, kBq \, h^{-1})$ was released through the water effluent $(11 \times 10^3 \, kBq \, h^{-1})$, while a flow of $7 \times 10^3 \, kBq \, h^{-1}$ was associated to the sludges pathway. Only a very small portion $(1.7 \times 10^3 \, kBq \, h^{-1})$ precipitated with the DCP (Fig. 4). As observed in Fig. 5, ^{226}Ra follows the $CaCl_2$ flux, agreeing with the work published by Gäfvert et al. [7]. However, in the case studied by Gäfvert et al. [7], $CaCl_2$ was collected and purified for other industrial uses, whereas in the plant under study here, $CaCl_2$ was released in the water effluent (WT-DCP). Part of the ^{226}Ra held in the WT-DCP was precipitated in the water treatment plant and driven to the general sludges, thus increasing both the specific concentrations and the general flux in the SG-GN compared to the SG-DCP. This also explains the ^{226}Ra drop from the WT-DCP effluent to the WT-GN one by a factor of two.

The fate of ^{226}Ra depends on the acid used for the phosphate rock digestion, since this radionuclide largely fractionates to wastes (phosphogypsum) when sulphuric acid is used, and only a small fraction remains in the acid flux [14,17]. However, the peculiarity of the mass balance of ^{226}Ra in this study was that the ^{226}Ra inflow was not equal to the sum of the outflows (i.e. the OIR was 0.66 ± 0.09), similarly than in Gäfvert et al. [7], with a missing amount of about $(10 \pm 4) \times 10^3 \, kBq \, h^{-1}$. Two hypotheses were formulated to explain this imbalance. The first one was that Ra might recirculate into the system and subsequently accumulate in the industrial process. The recirculation line (RE) carried about 10% of the total input of ^{226}Ra, which might partly explain the missing Ra if accumulation was eventually occurring in the succeeding steps of the recirculation flow. The second hypothesis was that Ra might precipitate in the digesters, where scales consisting of sulfates form deposits. Results on the scales collected in the digesters of the industry presented in this work are shown in Fig. 6. Specific activities of ^{226}Ra in the scales ranged widely, depending on where they crystallize within the digester. The lowest activities $(302 \pm 37 \, Bq \, kg^{-1})$ correspond to the scales formed in the DCP crystallization stage (white scales) collected at the precipitation tanks (sample 5), while the highest activities $(115 \times 10^3 \, Bq \, kg^{-1})$ were found in precipitates collected from the walls of the digester tanks (sample 7). Beddow et al. [19] suggested that these scales may be formed of calcium sulphate, fluorides and an assemblage of mixed fluorides and phosphates that precipitate during the digestion of the phosphate rock with an acid, remaining attached to the digester walls. However, the concentra-
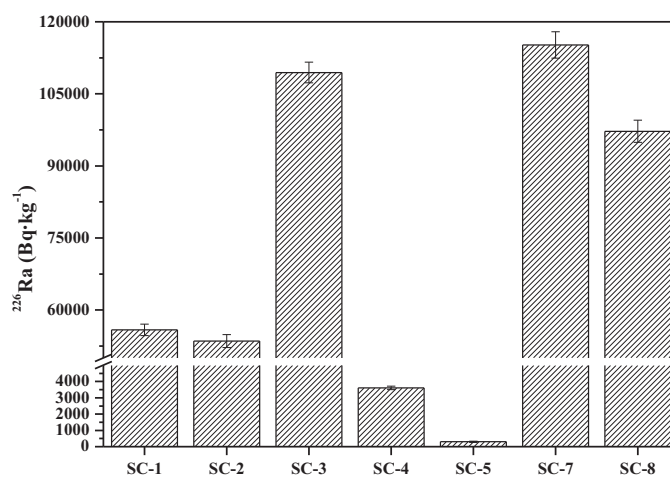
tions of ^{226}Ra in scales measured in the present work are about one order of magnitude higher than in the study published by Beddow et al. [19]. Conversely, these results matched up with those reported in other studies where scales formed in oil and gas industries were analyzed [20–22].

Assuming that the reaction surface is $500 \, m^2$ and accumulates a layer of scales of about 3 cm thick each year, an approximate rate of scale formation could be calculated. If the scale density is $2 \, t \, m^{-3}$, the annual scale rate formation would be of about $30 \, t \, y^{-1}$, which would explain between 4 and 7% of the ^{226}Ra deficit.

Both the accumulation of ^{226}Ra in the scales formed on the digester walls and the ^{226}Ra released in the water effluent would not represent harm neither to the workers, nor to the environment. On the one hand the company informs that surveys of gamma external dose to workers carried out show that dose limits established in the Euratom 29/96 $(1 \, mSv \, y^{-1})$ are not surpassed. On the other hand the input of ^{226}Ra to the river would not imply a substantial increase of its natural concentrations, since in this particular case the river flow is at least three orders of magnitude greater than the water effluent.

3.4. Lead

Specific concentrations of ^{210}Pb during the DCP production process point to a heterogeneous distribution along the industrial stages. The initial concentration found in the phosphate rock (PR) was $1890 \pm 216 \, Bq \, kg^{-1}$, and was decreased to $283 \pm 11 \, Bq \, kg^{-1}$ after digestion (PRAD). Dilution of the specific concentration of ^{210}Pb was not as high as for U and Th, since a recirculation flow from the tank 2 might enhances the ^{210}Pb activity at this stage. Indeed, this is corroborated with samples NDPR and SG-DCP: the concentration of ^{210}Pb in the non-digested fraction of the phosphate rock (NDPR) was of $404 \pm 92 \, Bq \, kg^{-1}$, which is twice the activity found in the sludge (SG-DCP) $(232 \pm 80 \, Bq \, kg^{-1})$. The highest activity for ^{210}Pb was observed in the DCP $(2003 \pm 169 \, Bq \, kg^{-1})$, followed by the general sludge (SG-GN) $(1236 \pm 168 \, Bq \, kg^{-1})$ and the recirculation flow (RE) $(587 \pm 29 \, Bq \, kg^{-1})$.

In terms of fluxes (Table 2), a large fraction $(25 \times 10^3 \, kBq \, h^{-1})$ of the total ^{210}Pb inflow $(34 \times 10^3 \, kBq \, h^{-1})$ was released in the DCP, and only $4 \times 10^3 \, kBq \, h^{-1}$ were held in the sludges (SG-DCP). Thus, 75% of the ^{210}Pb inflow was found in the DCP whereas 12% was held in the sludges (Fig. 4). As for ^{226}Ra, the ^{210}Pb outflows were enhanced in the general sludges $(10 \times 10^3 \, kBq \, h^{-1})$ compared to
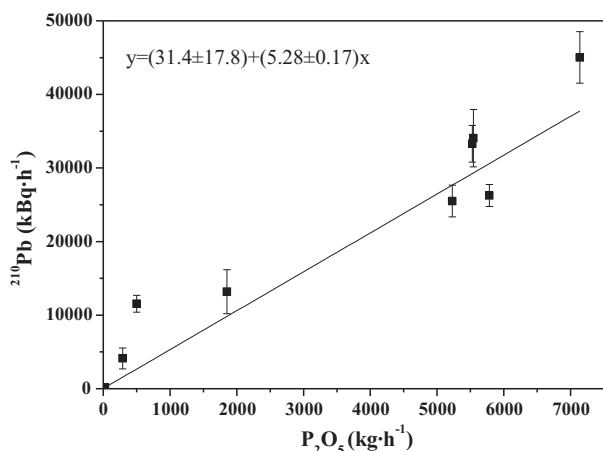
Fig. 7. ^{210}Pb flow versus P$_2$O$_5$ flow in samples collected at different stages of the DCP production process. $R^2 = 0.90$ and $p < 0.001$.

the sludges coming from the waste line (4×10^3 kBq h^{-1}), and the activity in waters was diluted after the water treatment plant (from 167 kBq h^{-1} to 13 kBq h^{-1}). Therefore, the water treatment plant played an important role in decontaminating ^{210}Pb and ^{226}Ra in waters (WT-GN), by precipitating these radionuclides and driving them to the general sludges flow (SG-GN). In general terms, it was observed that the OIR for ^{210}Pb did not deviate from unity (0.87 ± 0.13).

Results on ^{210}Pb fluxes slightly differ from those reported by Gäfvert et al. [7], where ^{210}Pb was uniformly distributed between the various products and wastes (i.e. DCP, sludges and CaCl$_2$). These differences relay on the fact that the production process studied here is constantly oversaturated in Pb due to the existence of a recirculation flow (RE), which carries 12×10^3 kBq h^{-1}, representing a 34% of the total ^{210}Pb. Although in acidic environments Pb^{2+} would normally be found in solution [23], the oversaturation of Pb in the system forces its precipitation both in the form of phosphate (Eq (3)) and as CaF$_2$.

$$Pb^{2+}(HPI_4)^{2-} \rightarrow PbHPO_4 \qquad (3)$$

Whereas if Pb was found in solution it would be brought back to the DCP production line, the actual conditions of oversaturation of Pb in this plant make it follow the sludge line. However, a fraction of ^{210}Pb that precipitates as CaF$_2$ may be redissolved in the form of CaCl$_2$ in the decanter tank 2 and thus recirculated to the initial digester. Due to this oversaturation of ^{210}Pb in the inner system, a good correlation ($R^2 = 0.90$, $p < 0.001$) was observed between fluxes of P$_2$O$_5$ and ^{210}Pb (Fig. 7). This is a particularity of the system described in this work compared to other studies in which the correlation P$_2$O$_5$ was observed with uranium instead of lead [14,24].

3.5. Polonium

The chemical pathways of ^{210}Po were similar to those of ^{230}Th. Initial concentration found in the phosphate rock (PR) was 1855 ± 263 Bq kg^{-1}, which were diluted to 182 ± 11 Bq kg^{-1} after digestion of the raw material (PRAD). The non-digested fraction of the phosphate rock (NDPR) presented higher specific activities (771 ± 25 Bq kg^{-1}) than the digested fraction (DPR) (8.2 ± 0.4 Bq kg^{-1}), ending at the final sludges (SG-DCP) with a specific concentration of 1634 ± 31 Bq kg^{-1}. The DCP production carried a small fraction of the ^{210}Po inflow, leading to an end-product (DCP) that had 100 ± 4 Bq kg^{-1}. The highest ^{210}Po activity was found in the general sludges (SG-GN) (4224 ± 145 Bq kg^{-1}), as for the case of ^{230}Th.

Regarding fluxes of ^{210}Po, it was observed that a large fraction (29×10^3 kBq h^{-1}) of the total ^{210}Po inflow (33×10^3 kBq h^{-1}) was discharged in the form of sludge, and a small fraction did it in the DCP (1.2×10^3 kBq h^{-1}) (Fig. 4). Therefore, the ^{210}Po fluxes basically follow the CaF$_2$ pathway, similarly to ^{230}Th (see Table 1). The output to input ratio (OIR) fairly approached the unity (0.91 ± 0.13), thus giving an optimum picture of the ^{210}Po fluxes.

The ^{210}Po results obtained here differ from those obtained by Gäfvert et al. [7], who found that only 30% of the ^{210}Po coprecipitated with the DCP, while no information on ^{210}Po accumulation in sludges was provided. Other studies in which phosphate rock was digested with sulphuric acid found that 98% of ^{210}Po was scavenged from the acidic solution and precipitated with the phosphogyspum waste [16], indicating that this radionuclide is generally eliminated through wastes, regardless of the acid used for the digestion of the phosphate rock.

4. Conclusions

The radionuclide fluxes of the ^{238}U decay series in the DCP production process (via HCl) of a European phosphate industry plant were studied herein. Secular equilibrium conditions of the radionuclides determined in the phosphate rock ($\sim$1700 Bq kg^{-1} of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po) were disrupted after the digestion of the raw material. However, radionuclides did not distribute homogeneously between production lines: ^{238,234}U and ^{210}Pb presented the greatest activities (1500–2000 Bq kg^{-1}) in the product, while ^{230}Th and ^{210}Po were enhanced in the sludges (1600–2000 Bq kg^{-1}). ^{226}Ra was distributed more homogeneously, presenting particularly high concentrations in waste waters (48×10^3 Bq m^{-3}) and in the scales formed in the digester (up to 150×10^3 Bq kg^{-1}). Fluxes of radionuclides were calculated and the output to input ratios (OIR) showed a reasonable mass balance calculation in all cases (i.e. did not deviate from unity). Thus, ^{238}U and ^{234}U outflows are equally distributed between sludges (16×10^3 kBq h^{-1}) and dicalcium phosphate (20×10^3 kBq h^{-1}); ^{230}Th and ^{210}Po were wholly discharged through the sludges (30×10^3 kBq h^{-1}). Conversely, the greatest ^{210}Pb outflow was the dicalcium phosphate current (25×10^3 kBq h^{-1}) and ^{226}Ra was mainly discharged through the water effluent (12×10^3 kBq h^{-1}) and to a lesser extent to the sludges (7×10^3 kBq h^{-1}).

This study corroborates the convenience of the inclusion of DCP industries in the positive list of NORM industries detailed in the revised version of the EU-BSS for protection against ionizing radiation and for the safety of radiation sources (EURATOM 29/96). Moreover, the results stress the importance and necessity of monitoring the phosphate industries, since even minor differences in the production processes lead to diverse activity concentrations in products and wastes, as observed in this study when compared to the work conducted by Gäfvert et al. [7] in a similar but not identical industrial process.

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