1. Introduction

Due to the relatively high concentration of \( ^{238}\text{U} \) (and its decay chain daughters) in phosphate rocks (PR), phosphate industries constitute one of several minerals related industry sectors for which some of the processes involved may warrant radiation protection measures through the system of regulatory control for practices (IAEA, 2013), also known as Naturally Occurring Radioactive Material (NORM) industries. The activities of these industries regarding radiation are now regulated in Europe by the European Directive 2013/59/EURATOM (EURATOM, 2013). Both legislations establish uniform basic safety standards for the protection of the health of individuals subject to occupational, medical and public exposures against the dangers arising from ionizing radiation (EURATOM, 2013).

Phosphate deposits contain calcium and phosphorus and can be of sedimentary marine, igneous, metamorphic or biogenic origin (IAEA, 2013), although the majority of the phosphate production plants use sedimentary marine deposits. This is the case of Morocco, from where the European phosphate plants obtain the phosphate rock as raw material. Typical activity concentrations of \( ^{238}\text{U} \) in these deposits are 1600 - 1700 Bq·kg\(^{-1}\) (in equilibrium with decay progeny) (Azouazi et al., 2001). These concentrations are of about two orders of magnitude higher than average concentrations in natural soils (30 Bq·kg\(^{-1}\); UNSCEAR, 2000), and in PR from igneous origin (e.g. Kola (Russia), 40 Bq·kg\(^{-1}\) of \( ^{238}\text{U} \) and 30 Bq·kg\(^{-1}\) of \( ^{232}\text{Th} \)) (Sabiha-Javied et al., 2010).

Once in the plant, phosphate ore is converted into commercial products. In most cases (85%) the PR is acid digested (wet process) and is later converted into intermediate or final products, including phosphoric acid (70%), and a variety of other products such as animal feed supplements (i.e. Dicalcium Phosphate, DCP) (IAEA, 2013).

During the industrial processing of these materials, exposure to gamma radiation from radionuclides of the \( ^{238}\text{U} \) decay series is the main concern for radiation protection. However, exposure to radionuclides in inhaled dust particles can also be relevant (IAEA, 2013), and has been investigated in various phosphate industries (Papastefanou, 2001; San Miguel et al., 2009). \( ^{222}\text{Rn} \) can also emanate from accumulated \( ^{226}\text{Ra} \) (White and Rood, 2001) and may also be responsible for a significant fraction of the total dose to workers. Gamma-radiation dose rates are generally higher near digestion tanks, piping, filters and residual stockpiles, due to radionuclide accumulation, increasing the ambient equivalent dose (Gäfvert et al., 2001; Bolívar et al., 2009). Therefore, the manipulation and treatment of the phosphate rock ore and the different by-products could lead to an increase of the radiological doses to workers.

The industrial plant studied here produces dicalcium phosphate (DCP) used as an inorganic feed supplement for farm animals (Casacuberta et al., 2009; 2011). Differently to most of the phosphate plants that use sulfuric acid to digest the PR, hydrochloric acid is used in this plant (Casacuberta et al., 2011). Previous studies in the same plant were focused on the radiological fluxes of the production process, showing
that the equilibrium between the radionuclides of the $^{238}$U decay series is disrupted due
to the different chemical behavior after the PR digestion with hydrochloric acid
(Casacuberta et al., 2011) and they are distributed in different proportions in the final
product and by-products, Casacuberta et al. (2011) also described the accumulation of
significant amounts of $^{226}$Ra in pipes during the DCP production process that can
increase the external gamma-radiation dose to workers in the plant.

The aim of this study is to establish a radiological risk assessment to the workers of the
DCP industry. Several surveillances in the DCP plant were carried out between 2011
and 2014 to determine the concentrations of the most significant radionuclides in
aerosols, the $^{222}$Rn concentrations in air and to map the gamma-radiation dose rates.
External and internal doses were assessed for workers in order to determine whether
annual doses exceed the 1 mSv·y$^{-1}$ limit reference value established by the European

2. Materials and Methods

2.1 Description of the DCP production plant

The plant is located in the Iberian Peninsula (Europe) and nowadays it has a total
production capacity of 360 t of DCP per day. The production process can be divided
into three main lines (sludge, DCP and water effluents), and therefore wet and dry
production areas can be identified (Figure 1). Details are described in Casacuberta et al.
(2011). Most steps of the production process are located outdoors, although there are
some indoor areas such as offices, control areas, packaging store and milling area. Wet
process areas in the sludge line include the PR digestion area and the decantation area.
In the DCP line, the precipitation and filtering areas are also wet process areas. The dry
process areas are the PR milling in the sludge line and the DCP drying, loading and
packaging areas in the DCP line.

2.2 Sampling, measurements and data collection

The criteria used to design the sampling procedure of aerosols, Rn measurements and
and ambient dose equivalent H*(10) was considering the most occupied workplaces and
transiting areas by plant operators.

2.2.1 Aerosols

Sampling of aerosols was carried out in November 2011 and March 2012 at 8 different
locations of the DCP production plant (Fig. 1). Between 10 - 30 m$^3$ of air were filtered
using a SAIC Radeco vacuum-pump system at 25 cm above the ground. Aerosol
particles ($>0.3 \mu$m) were retained onto pre-weighted glass fibre filters (LB-5211 type,
Radeco). Filters were cut into two identical sections for the subsequent analysis of
radionuclides.
The equivalent to half of each sample was used to quantify the concentration of $^{210}\text{Pb}$ and $^{210}\text{Po}$, following the method described in Masqué et al. (2002). Briefly, the filter was first acid digested after addition of $^{209}\text{Po}$ as an internal tracer. The residue was dissolved in 100 mL of HCl 1N and polonium isotopes were auto-plated onto 2.2 cm silver discs for 6 – 7 h at 70 ºC with constant stirring. Any polonium activity remaining in the solution was removed by a second deposition onto silver discs, re-spiked with $^{209}\text{Po}$ and stored for more than 6 months. The $^{210}\text{Pb}$ concentration was obtained after a second plating and measurement of the ingrowth of $^{210}\text{Po}$. The silver discs were measured using a Canberra Alpha Analyst spectrometry system equipped with Passivated Implanted Planar Silicon (PIPS). The determination of the initial activities of $^{210}\text{Pb}$ and $^{210}\text{Po}$ were carried out following Rigaud et al. (2013).

The other half-filter sections were used for the quantification of $^{238}\text{U}$ and $^{230}\text{Th}$, also by alpha spectrometry. The radiochemical separation of U and Th, was carried out by extraction chromatography using UTEVA resins and electrodeposition onto 2.2 cm diameter silver discs, as described in Casacuberta et al. (2012). $^{232}\text{U}$ and $^{229}\text{Th}$ were used as internal yield tracers.

2.2.2 Atmospheric $^{222}\text{Rn}$

Measurements at 9 indoor and 22 outdoor sites were carried out using passive positioned between 50 and 100 cm above the ground and active $^{222}\text{Rn}$ detectors (25 cm above the ground) during two different periods: 18 – 19 July and 8 – 9 November 2011. We used the Karlsruhe®FN dosimeters based on Makrofol®DE for the passive measurements of integrated $^{222}\text{Rn}$ concentrations in 7 indoor and 7 outdoor sites. After four months of exposure, detectors were collected and the Makrofol foils were electrochemically etched with laboratory standard conditions. The track counting was performed with a semi-automatic system. These detectors were calibrated at the Public Health England (PHE) radon chamber, for which the calibration factor is regularly checked by participating in national and international comparisons. The detection limit ($D_L$) for a four month measurement period was 9 Bq·m$^{-3}$ (Moreno et al., 2008). Polyethylene membranes were used to protect radon detectors from environment conditions (high dust concentration and humidity) (Moreno et al., 2013; 2015).

An AlphaGuard monitor (Saphymo GmbH), consisting of an ionization chamber, and a RAD 7 monitor (Durridge Co), consisting of an electrodepositing chamber with a semiconductor, were used for monitor continuously the $^{222}\text{Rn}$ concentration at 3 indoor sites (service, rock discharge and packaging buildings) from 12 h to 18 h, integrating the data in 30 min intervals. The RAD 7 monitor was also used to perform short timescale measurements (about 1 h) at all the other sites.

2.2.3 Gamma-radiation dose rates
Three campaigns to determine external gamma-radiation dose rates were carried out in July 2011, November 2011 and May 2012 at various locations of the DCP production plant (50 cm above the ground), using an Eberline E-600 connected to a SHP-270 probe, calibrated for measuring ambient dose equivalent \( H^*(10) \). Pipes were also measured in order to determine the \(^{226}\text{Ra}\)-derived dose with a Canberra Inspector 1000 equipped with a gamma NaI(Tl) probe. Personal equivalent dose \( H_p(10) \) was measured during the pipe removal and maintenance in February 2014, using an electronic personal dosimeter, Dosicard (Canberra).

2.3 Dose assessment quantification

The operational annual effective above background dose received by the plant operators was calculated considering the sum of annual occupational exposures of a worker according to the European Directive 1996/29/EURATOM (EURATOM, 1996).

\[
E = E_{\text{External}} + \sum_j (h(g)_{j,\text{inh}} \cdot J_{j,\text{inh}}) + \sum_j (h(g)_{j,\text{inh}} \cdot J_{j,\text{inh}}) + E_{\text{Rn}} \tag{1}
\]

where \( E_{\text{External}} \) is the corresponding effective dose from external exposure and \( \sum_j (h(g)_{j,\text{inh}} \cdot J_{j,\text{inh}}) \), \( \sum_j (h(g)_{j,\text{inh}} \cdot J_{j,\text{inh}}) \) are the committed effective doses due to ingestion and inhalation, respectively, and \( E_{\text{Rn}} \) is the operational annual effective dose due to the \(^{222}\text{Rn}\) inhalation. Given the characteristics of the studied site, the exposure due to ingestion is considered negligible (IAEA, 2013). \( h(g)_{j,\text{inh}} \) (in Sv·Bq\(^{-1}\)) is the committed effective dose per unit-intake for inhaled radionuclide \( j \) by an individual in the group of age \( g \) and \( J_{j,\text{inh}} \) (in Bq) is the relevant intake via inhalation of the radionuclide \( j \) in a year. According to Article 9 of EURATOM (2013), the occupational exposure to \(^{222}\text{Rn}\) inhalation in workplaces needs to exceed the national reference level (300 Bq·m\(^{-3}\)) to be considered in the operational annual effective dose, which is then calculated according to UNSCEAR (2000).

The estimate of the internal dose by inhalation was carried out only for radionuclides of the \(^{238}\text{U}\) decay series using the conversion factors from the ICRP (2012): 1.6·10\(^{-6}\) Sv·Bq\(^{-1}\) for \(^{238}\text{U}\), 2.8·10\(^{-5}\) Sv·Bq\(^{-1}\) for \(^{230}\text{Th}\), 1.1·10\(^{-6}\) Sv·Bq\(^{-1}\) for \(^{210}\text{Pb}\) and 2.2·10\(^{-6}\) Sv·Bq\(^{-1}\) for \(^{210}\text{Po}\). These parameters correspond to an activity median aerodynamic diameter (AMAD) of 5 µm and to the M class (intermediate rate of absorption) except for \(^{210}\text{Pb}\), for which the default class was F (fast rate of absorption).

3. Results and Discussion

3.1 Aerosols

Concentrations of \(^{238}\text{U}\) (in equilibrium with \(^{234}\text{U}\)), \(^{230}\text{Th}\), \(^{210}\text{Pb}\) and \(^{210}\text{Po}\) in aerosols determined at different locations in the DCP plant are shown in Table 1. Results were
divided into “wet process” and “dry process” locations, as it would be expected to find
less airborne dust particle in the former compared to the latter. Indeed, locations in the
“dry process” areas (F3, F4 and F8) had mean concentrations of 51 mg·m⁻³ while “wet
process” locations (F1, F2, F6 and F7) and service building averaged 2 mg·m⁻³,
respectively. This is due to the fact that dust accumulates mainly in storage and milling
of PR areas, as well as in DCP storage areas. Activity concentrations of ²³⁸U ranged
from 0.36 ± 0.03 to 92 ± 5 mBq·m⁻³, with the highest concentration detected in the DCP
loading trucks area. The same trend was observed for ²¹⁰Pb with values ranging between
0.67 ± 0.04 and 147 ± 6 mBq·m⁻³. In the case of ²³⁰Th and ²¹⁰Po, the range of values
were between 0.24 ± 0.04 and 33 ± 2 mBq·m⁻³ and between <0.007 and 34 ± 6 mBq·m⁻³,
respectively, with the maximum concentration measured in the PR milling area. In
general, the highest activity concentrations in aerosols were observed in the “dry
process” locations such as storage and milling of PR areas and DCP storage areas
because those areas have more suspended aerosol concentrations (see Table 1).

Samples collected in the PR milling area (F-3) showed activity ratios close to unity
(Table 1). This corroborates that dust particles in this location (43 mg·m⁻³) are
composed of PR. On the other hand, the airborne dust particle in loading trucks (F-8)
and packaging areas (F-4) (91 and 18 mg·m⁻³, respectively) had higher concentrations
of both ²³⁸U and ²¹⁰Pb compared to ²³⁰Th and ²¹⁰Po. These concentrations are in
agreement with the radionuclide activity ratio of DCP (Table 1), described in
Casacuberta et al. (2011). The ²¹⁰Pb/²¹⁰Po ratio in the packaging area (1.7 ± 0.3) reflects
the ingrowth of ²¹⁰Po from the decay of ²¹⁰Pb present in old DCP dust accumulated
around the area.

Aerosol samples collected in the “wet processes” areas were less enriched in
radionuclides. Samples with the lowest activities (F-1 and F-2) showed slightly higher
specific activities above the measured background for ²³⁸U and ²¹⁰Po (Table 1) and for
the range reported by Preiss et al. (1996) for ²¹⁰Pb of 0.2 - 0.5 mBq·m⁻³ in Europe.
Samples located in the digestion section (F-6 and F-7), that are also outdoor locations,
showed higher concentrations of ²¹⁰Pb (5.5 ± 0.3 and 1.69 ± 0.08 mBq·m⁻³,
respectively) compared to the rest of the wet process areas. This may be related to the
highest ²²²Rn concentration measured in the digestion and decanter areas in the DCP
plant (Table 2), adding to the ²¹⁰Pb naturally present in air and DCP suspended dust.
Thus, the ratios obtained for the wet process areas sampling points F-6 and F-7 were not
exactly in agreement with PR and DCP dust ratios.

The concentrations in aerosols collected in the office and the service building (F-5)
were higher than in most locations at the wet processes areas, especially for ²³⁸U, ²¹⁰Pb
and ²¹⁰Po, likely due to the spreading of DCP dust originating from the nearby DCP
drying facility. However, because the presence of old DCP accumulated in the area
allows ingrowth of ²¹⁰Po when in the packaging area, the ²¹⁰Pb/²¹⁰Po ratio in this sample
is lower than the DCP ratio (Table 1).
3.2 Atmospheric $^{222}$Rn

$^{222}$Rn concentrations in air measured with the passive detectors ranged from $<D_L$ (9 Bq·m$^{-3}$) to 211 ± 61 Bq·m$^{-3}$ (Table 2). This maximum value corresponds to the indoor sludge line area where the phosphate rock ore is denaturalized, milled and dissolved with hydrochloric acid. Complementary measurements taken with active detectors in the same area confirm this result: the highest $^{222}$Rn mean values of 186 ± 16 Bq·m$^{-3}$ (July 2011) and 318 ± 58 Bq·m$^{-3}$ (November 2011) were obtained in the 1st and 2nd underground floors, respectively, where the PR is discharged, stored and milled. The use of active detectors also highlight the fact that, respect to 1st underground floor, maximum punctual levels of 760 ± 98 Bq·m$^{-3}$ in July 2011 (Figure 2A) and 480 ± 80 Bq·m$^{-3}$ in November 2011 (Figure 2B) were reached. In addition to the possible natural background contribution (10 Bq·m$^{-3}$, UNSCEAR, 2010), this high concentration in the two floors air of the semi-closed corridors under the silos is due to the easily $^{222}$Rn exhalation from the accumulated PR powder produced during the milling process. Passive measurements next to the open top of the digester tanks (Table 2; P15) also registered significantly high $^{222}$Rn concentration (121 ± 17 Bq·m$^{-3}$) compared to the other outdoor areas in the sludge line where maximum values did not exceed 25 Bq·m$^{-3}$. This high outdoor $^{222}$Rn concentration on top of the digesters is attributed to the boiling process that occurs during the HCl chemical reaction with the PR, leading to $^{222}$Rn release to the air. Results of the active measurements did not reach the highest value measured in the digester tanks with the passive measurements. However, the concentration in the 1st floor of the milling area (67 ± 29 Bq·m$^{-3}$) suggests that the $^{222}$Rn emanation may also occur, although to a lesser extent, in the decantation area. Outdoor $^{222}$Rn concentrations in the rest of the sludge line area were, in general, higher (from $<D_L$ to 47 ± 18 Bq·m$^{-3}$) than the world mean value for outdoor areas (10 Bq·m$^{-3}$, UNSCEAR, 2010).

$^{222}$Rn concentrations measured with passive detectors (long-term or integrated measurements) in the DCP line ranged from $D_L$ to 48 ± 10 Bq·m$^{-3}$. The complementary short timescale measurements with active detectors showed mean values similar to the integrated measurements, with activity concentrations that ranged from $<D_L$ to 52 ± 19 Bq·m$^{-3}$, with the highest measurements recorded in those areas located next to the sludge line area (precipitation and filtering areas). These concentrations of $^{222}$Rn in air above the natural background in the DCP production plant may be due to: (i) the scales formation with $^{226}$Ra (Casacuberta et al., 2011) that leads to $^{222}$Rn emanation, as shown in previous studies in NORM industries (White and Rood, 2001) and the $^{222}$Rn emanation due to $^{226}$Ra accumulation in ebonite, and; (ii) the emanation of $^{222}$Rn from the phosphate rock ore processing in the milling and digestion.

Indoor areas such as services and office building areas, where workers spent most of their working hours, registered mean $^{222}$Rn concentrations below 300 Bq·m$^{-3}$. $^{222}$Rn concentrations measured with passive detectors were 152 ± 20 Bq·m$^{-3}$ in the laboratory and 180 ± 22 Bq·m$^{-3}$ in the control room (Table 2). Those values agree with the concentration measured with the active detectors in November 2011 with mean values
of 193 ± 47 Bq·m⁻³ in the office and 203 ± 84 Bq·m⁻³ in the laboratory. Results obtained with active detectors in July 2011 were generally lower with mean values of 48 ± 36 Bq·m⁻³ and 43 ± 24 Bq·m⁻³, respectively. Maximum punctual values recorded with active detectors were 285 ± 55 Bq·m⁻³ in July 2011 in offices (Figure 2C) and 459 ± 68 Bq·m⁻³ in the laboratory (Figure 2D).

3.3 Gamma-radiation dose rates

The ambient dose equivalent H*(10) values measured in the DCP production plant are listed in Table 3 and it is shown in Figure 3. Doses in the DCP line were generally low, ranging from background (0.05 – 0.08 µSv·h⁻¹) to 0.57 µSv·h⁻¹. The highest doses were recorded in the sludge line (up to 27 µSv·h⁻¹), particularly in the digestion and the decantation areas of the plant and in the scrap metal disposal controlled area, where pipes and metal devices from the DCP plant have been accumulated after its substitution in the production plant.

In the digestion area, the walls of the digesters tanks tend to accumulate ²²⁶Ra due to scales formation (Casacuberta et al., 2011). Scales composition is determined by the particular chemical conditions of the different production stages (Beddow et al., 2006) and it is usually characterized by conglomerates of calcium sulphate, fluorides and phosphates that include a fraction of dissolved ²²⁶Ra and their daughters in the crystalline structure. Gamma-radiation doses ranged from 0.87 to 4.1 µSv·h⁻¹, increasing at closer distances to the digesters tanks, being highest in contact with those digesters that accumulated waste muds (4.1 µSv·h⁻¹) (Figure 3, A3), followed by the values measured in contact with the walls of the digestion tanks (3.5 µSv·h⁻¹ in the first floor and 3.3 µSv·h⁻¹ in the second floor). Several zones close to the digestion area were also influenced by the presence of ²²⁶Ra. Gamma-radiation doses in the milling area were higher than background, with values ranging from 0.10 to 0.31 µSv·h⁻¹, the highest in the vicinity of the digestion area.

In the decantation area, gamma-radiation doses measured close to pipes internally coated with ebonite were significantly high, ranging from 0.23 to 27 µSv·h⁻¹. Ebonite is a type of rubber used to protect the pipes from acid corrosion. The maximum values of 13 and 27 µSv·h⁻¹ were obtained in contact with the pipe that connects decanter tank 1 with decanter tank 2 (Figure 3, A1) and in contact with the pipe from decanter tank 1 to re-digestion tank 1A (Figure 3, A2), respectively. The measurements of gamma-radiation doses with NaI(Tl) and the visual inspection of some dismantled pipes confirmed the presence of large amounts of ²²⁶Ra in the ebonite and the absence of scales, suggesting that the use of ebonite enhances the accumulation of ²²⁶Ra inside the pipes. The measurement of pipes extracted from the production process revealed that those internally coated with ebonite presented doses of 0.18 - 13 µSv·h⁻¹, while pipes that were not coated with ebonite showed values similar to the background (up to 0.08 µSv·h⁻¹) (Table 4). Relatively high doses were measured in some other zones in the decantation area, such as in the sludge compressor area (4.8 µSv·h⁻¹, Fig 3, A6), likely
due to the high concentrations of $^{226}\text{Ra}$ in sludge and fluids present in this area (Casacuberta et al., 2011).

In the precipitation and filtering zones located in the wet DCP line area the doses ranged from 0.19 to 0.54 $\mu$Sv·h$^{-1}$, substantially lower than in the digestion and decantation areas (Table 3). Doses slightly above background could be caused by white scales formation with low concentrations of $^{226}\text{Ra}$ (Casacuberta et al., 2011) or by the adjacent sludge line.

In drying, storing and services areas (Table 3) the values obtained are comparable to background (from background to 0.13 $\mu$Sv·h$^{-1}$) and the apparent faint increment may be caused by the $^{226}\text{Ra}$ accumulation in the adjoining areas from the plant, without significantly contributing to the external dose to workers, although they spend most of their working time in this area.

Finally, outside the DCP production plant area (Fig 3. A4), dismantled pipes with ebonite and devices extracted from the plant due to maintenance operations provide also gamma-radiation dose levels above background due to the accumulation of $^{226}\text{Ra}$ after being used in the DCP plant for several years. The median ambient dose equivalent $H^*(10)$ was 1.0 $\mu$Sv·h$^{-1}$, with maximum values around 8.1 $\mu$Sv·h$^{-1}$ (Fig 3, A4) in contact with scrap containers or pipes.

### 3.4 Occupational Effective Dose

In order to estimate the occupational dose to DCP plant workers, two types of working tasks are considered: i) those related to operators that check routinely the correct functioning of the plant and; ii) those related to workers that carry out maintenance tasks of the plant, such as cleaning and fixing tanks and pipes. Both types of operators are exposed to external radiation, airborne dust particle and $^{222}\text{Rn}$ inhalation. In both cases the committed effective dose due to the inhalation of aerosols was quantified using the concentrations of $^{238}\text{U}$, $^{230}\text{Th}$, $^{210}\text{Pb}$ and $^{210}\text{Po}$ and a breathing flux of 1.2 m$^3$·h$^{-1}$ (ICRP-66; 1994). The sample F1, collected at the stairs next to Digester-2 on the 3rd floor, was considered as background for the atmospheric particles inhalation dose source (Table 5).

#### 3.4.1. Plant Operators

Results of the occupational effective dose estimated for the plant operators that check routinely the correct functioning of the plant are shown in Table 5. Doses were quantified using the annual occupation time of each worker in the different areas within the DCP production plant (Table 5).

The effective external dose ranges from 0.08 to 0.16 mSv·y$^{-1}$, being the highest in the sludge line due to the accumulation of $^{226}\text{Ra}$ in the ebonite and pipes (scales). Although
the external dose rates are generally high in the DCP line, the limited time that operators spend in the area results in an annual external dose to workers of 0.08 mSv·y⁻¹. The external dose measured in the services area is slightly higher (0.11 mSv·y⁻¹) due to the greater occupational time of workers in this area.

The committed effective doses due to inhalation of airborne dust particles are significantly lower than the external dose, ranging from <0.01 to 0.02 mSv·y⁻¹. On the other hand, because the annual mean ²²²Rn concentration in workplaces does not exceed the European legislation reference level (300 Bq·m⁻³), the occupational exposure to ²²²Rn inhalation is not considered in the total operational annual effective dose.

The total occupational annual effective dose to workers (internal and external) resulted into 0.37 mSv·y⁻¹. Although the DCP and sludge lines presented greater dose rates during the short timescale measurements (Table 5), the limited time spent by workers in these areas limited its contribution to the annual doses. The occupational annual effective dose derived from the external dose and inhalation of aerosols obtained in the DCP production plant is higher than the 0.17 mSv·y⁻¹ (inhalation of aerosols 0.07 mSv·y⁻¹ and external dose ~ 0.10 mSv·y⁻¹) reported by Gäfvert et al. (2001) in a phosphoric acid plant in Sweden where PR is also digested with hydrochloric acid. On the other hand, Bolívar et al. (2009) estimated a total gamma-radiation external dose of less than 0.5 mSv·y⁻¹ in a phosphoric acid production plant in Spain, where phosphoric rock is digested with sulphuric acid.

3.4.2 Maintenance operators

Although most of the work carried out by operators is mainly focused on the routine checking of process parameters, there are several maintenance works that are performed during short periods of time (few hours) in areas with high ²²⁶Ra concentrations (pipes or tanks). The two major maintenance operations in the sludge line areas were analyzed: i) the cleaning of the digesters and, ii) the substitution of pipes (Table 6). In the first case the accumulated external dose in 2 h was 2.2 µSv. The pipe substitution operation increased the external dose of workers by 5.0 µSv in 2 h. The short duration of these operations does not lead to a significant increase of the external dose of the workers.

4 Conclusions

This work presents the first comprehensive radiological risk assessment in a phosphate industry plant that produces Dicalcium Phosphate. This was carried out by considering the external gamma-radiation dose rates, the internal dose due to inhalation of airborne dust particles and the assessment of ²²²Rn concentration in air.

The highest external gamma-radiation dose rates (up to 27 µSv·h⁻¹) were measured in the digestion and decantation areas, mainly due to the formation of scales in the digestor tanks and pipes, and to the presence of ebonite, a rubber material used to protect the pipes from the acid corrosion. However, the limited time spent by workers in those
areas resulted in an effective gamma-radiation external dose of less than 0.16 mSv·y⁻¹.

Considering also the DCP line and service building, the total effective external dose for workers was 0.35 mSv·y⁻¹.

Inhalation of aerosols resulted in a negligible (<0.02 mSv·y⁻¹) committed effective dose to workers.

Concentrations of $^{222}\text{Rn}$ were measured using different methods (passive and active) in different locations within the plant. The highest mean concentrations ($211 \pm 61 \text{ Bq·m}^{-3}$) were found in indoor areas, where PR is discharged, stored and milled. Mean $^{222}\text{Rn}$ concentrations in the service building were relatively high (up to 180 Bq·m⁻³), especially in those measurements performed in November 2011. Mean $^{222}\text{Rn}$ concentrations were always below the European legislation reference level (300 Bq·m⁻³) and therefore the $^{222}\text{Rn}$ occupational dose was excluded in the total operational annual effective dose. However, $^{222}\text{Rn}$ concentrations were highly variable, with several short-timescale measurements (Figure 3) higher than 300 Bq·m⁻³, with a maximum punctual measurement of up to 750 Bq·m⁻³, which may require complementary studies to understand the temporal variability of $^{222}\text{Rn}$ in the DCP plant.

The results obtained for external dose and inhalation of aerosols in the DCP production plant resulted in a total occupational annual effective dose of 0.37 mSv considering an annual occupational time of 1720 h. This annual dose to workers in the DCP plant studied here is significantly lower than the limits established by the EURATOM (2013) for non-radiation workers and members of the public (1 mSv·y⁻¹). This study highlights the importance of performing dose evaluations in NORM industries in order to be able to apply the proper countermeasures (e.g. limiting the residence time to exposure areas, air ventilation, dust cleaning…) so that the dose to workers is as low as reasonably achievable (ALARA).

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6. References


Figures

Figure 1. Sampling locations of aerosols (dot, F#), passive (cross, P#) and active (circle, A#) integrated $^{222}\text{Rn}$ measurements in the DCP plant. Sampling at different plant levels from ground indicated in brackets.

Figure 2. Radon short timescale concentrations obtained during an hourly period with active monitors in different locations from the DCP plant.

A) (A.9) Rock discharge area (basement -2) Radon concentration obtained with the active monitor AlphaGUARD for 18 hours between 18$^{th}$ and 19$^{th}$ July 2011.

B) (A.9) Rock discharge area (basement -2) Radon concentration obtained with the active monitor AlphaGUARD for 18 hours between 8$^{th}$ and 9$^{th}$ November 2011.

C) (A.23) Office $^{222}\text{Rn}$ concentration obtained with active monitor RAD7 for 16 hours between 18$^{th}$ and 19$^{th}$ July 2011 (left figure) and for 13 hours between 8$^{th}$ and 9$^{th}$ November 2011 (right figure).

D) (A.24) Laboratory $^{222}\text{Rn}$ concentration obtained with active monitor RAD7 for 16 hours between 18$^{th}$ and 19$^{th}$ July 2011 (left figure) and for 14 hours between 8th and 9th November 2011 (right figure).

Figure 3. Ambient dose equivalent $H^*(10)$ rate in above ground level (A) and level 1 (B) form the DCP Plant (μSv·h$^{-1}$). Sampling points are indicated with dots. The most significant dose rates correspond to the pipe that connects decanter tank 1 with decanter tank 2 (A1), the pipe from decanter tank 1 to re-digestion tank 1A (A2), the sands from the digester tanks cleaning operations (A3), the dismantled pipes with ebonite and devices extracted from the plant (A4), the digester tanks (A5) and the sludge compressors (A6).

Tables

Table 1. Concentrations of $^{238}\text{U}$, $^{230}\text{Th}$, $^{210}\text{Pb}$ and $^{210}\text{Po}$ (mBq·m$^{-3}$) in aerosols at different locations in the DCP production plant. Isotope ratios were quantified for aerosols, raw material (PR) and final product (DCP).

Table 2. Indoor and outdoor mean radon concentrations obtained with short timescale (about 1 h) or continuous (about 18 h) measurements using active detectors (A) in July 2011 and November 2011. Radon concentrations measured by passive detectors (P) during a four months period (July-November 2011) are also shown.
Table 3. Median ambient dose equivalent H*(10) and range of values measured in several areas in the DCP plant.

Table 4. Ambient dose equivalent H*(10) in several pieces extracted from the production process. Detailed for each piece the ebonite containing.

Table 5. Occupational annual effective dose received by the plant operator in different areas of the production plant due to effective external dose and committed effective dose due to inhalation of aerosols.

Table 6. Dose evaluation for plant operators in two maintenance operations in the DCP plant.