An assay on the effect of preliminary restoration tasks applied to a large TENORM wastes disposal in the South-West of Spain

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Abstract

A large industrial wastes disposal site, where two phosphate rock processing plants release their wastes, located close to Huelva town (SW of Spain) has been partially submitted to restoration as a preliminary step in a possible decomissioning process. Due to the high natural radioactivity contents of these wastes, this repository is considered as a radiological anomaly, being actually considered as TENORM (Technically Enhanced Naturally Occurring Radioactive Materials). The efficiency of this restoration from the radiological point of view according to the new european regulatory framework was evaluated in this work.

The results allow to conclude that, a consequence of the partial restoration works, the external dose rate has been drastically reduced above the repository system. Nevertheless, special attention must be paid on the occupational factor to be applied to workers on the unrestored system. The application of a dosimetric model allows the prediction of the negative effects of using certain industrial wastes as a cover system in this restoration/mitigation task.

Keywords: Phosphogypsum, Th-isotopes, U-isotopes, Ra-isotopes, Radiation Protection, NORM, phosphate rock processing plants.

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1. Introduction

The situation of many industries and their associated wastes involved in the management of NORM (Naturally Occurring Radioactive Materials) has to be evaluated to guarantee the safety of the population and workers. NORM is defined as all naturally occurring radioactive materials where human activities have increased the potential risk for radiation exposure in comparison to the unaltered situation (Betti et al., 2004). This fact results especially clear after the introduction of the EURATOM'96/29 European Directive, which has been adapted to the Spanish law framework through the RD 783/2001 order. In this normative, the annual dose limit for population (non-occupationals) and workers (occupationals) are 1 mSv and 10 mSv, respectively.

A well-known example of NORM-related processes is that of the facilities devoted to the production of phosphate fertilizers. These are manufactured from phosphate rock, which contains high concentrations of radionuclides from ^{238}U-Series (Guimond and Hardin, 1989; Barisic et al., 1992; Rutherford et al., 1994). The ^{238}U concentration in phosphate rock is up to 100 times higher than in the average United Nations soil (UNSCEAR,2000).

Industrial processing of rock phosphate to manufacture phosphate fertilizers through the wet-acid process involves the production of phosphoric acid according to the following chemical reaction:

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O \rightarrow 6\ H_3PO_4 + 10\ CaSO_4 \cdot 2H_2O + 2\ HF$$

The major by-product is the so-called phosphogypsum (PG), consisting in a $CaSO_4 \cdot 2H_2O$ matrix. During the process, the different radioactive isotopes released from the raw material follow either the phosphate oxide or the generated by-product, according to their respective elementary chemical behaviours (Rutherford et al., 1996). Uranium present in the phosphate rock solubilises and goes into the phosphoric acid fraction and ^{226}Ra is co-precipitated with the phosphogypsum, which is usually stored in land surface areas close to the processing plants. The radioactivity fractionation has been well established in the literature. It has been found that the major rates of Ra and Po isotopes (about 90%), a large

rate of thorium isotopes (70%) and a minor fraction of U isotopes (~15%), follow the by-product (Bolívar et al., 1996).

Effluent discharges into the environment as well as the use of phosphate rocks as raw material in different industrial activities are possible sources of radiation exposures to the public and workers (Bigu et al., 2000; Papastefanou, 2001). Indeed, the Radium isotopes are considered to be the main contributors to radiation dose from natural sources (Lozano et al., 2003).

A large industrial wastes disposal site (Figure 1), where two phosphate rock processing plants release their wastes, located close to Huelva town (SW of Spain) has been partially submitted to restoration works as a preliminary step in a possible decomissioning process. **These fertilizer facilities commonly deal with phosphate ore from Morocco. The high content of this rock in U-series radionuclides has been already well-established (Bolívar et al., 1996).** The main objective of this paper is to evaluate the efficiency of the restoration from the radiological point of view according to the new european regulatory framework. The radiological state of the phosphogypsum stacks and their surroundings after the introduction of a technological restoration solution has to be evaluated. New results are shown, and a comparison against previous data has to be performed in order to evaluate the efficiency of the previously mentioned restoration/mitigation works.

In this way, the potentialities of that region for future uses are tested. This information should be considered not only from the law-frame point of view, but also it could serve in the case of the possible decommissioning of the industrial activity: it is expected that in the mid-term time, these facilities will be transferred to another place. Hence, the ground where the PG stacks are located actually could be used in the future for residence buildings. As a consequence, unexpected radiological concerns could be arised.

2. Materials and methods

2.1 Study area

The large industrial complex, which is located in the proximities of Huelva Town (SW of Spain, population of 150000 habitants), includes among others several plants dedicated to the extraction of Cu and/or Fe, production of sulphuric acid, an oil refinery and two phosphate rock processing plants (see Bolívar et al., 2000, 2002 for details). During the past 40 years, the different phosphate rock processing plants have released a total amount of about $90 \cdot 10^6$ tonnes of PG. In order to release the by-product from the facilities, two ways have been used until a recent date: 1) around 20% of the wastes produced by the phosphate rock processing plants have been released directly to the Odiel river, which conforms with the Tinto River the Huelva Estuary (Bolívar et al., 2000) ; 2) the remaining 80% have been pumped, mixed in a river water solution (up to 20% phosphogypsum), to be stored in phosphogypsum piles formed near the plants (Bolívar et al., 1995).

These gypsum stacks cover a surface about 1200 Ha actually. The average height above the natural salt-marshes is in the range of 5 m. Due to the previously mentioned high concentrations of natural radionuclides, these stacks are considered as a radiological anomaly. Indeed, their proximity to Huelva Town (less than 2 km) has generated intense social alarm. **At this time, this area is under the control, surveillance and responsibility of one of the** phosphate rock processing plants **(Fertiberia, SA). The access to this area is limited to the workers, being the working time kept to a minimum. However, it still has not been recognised as a radiologically controlled area according to the Spanish regulatory administration. Therefore, the doses received by workers are not submitted to control by the Spanish administration.**

The wastes released for forty years to the river and its surroundings have leaded to a clear enhancement of radionuclide concentrations from U-series radionuclides in different compartments of the area (Bolívar et al.,2000; Bolívar et al., 2002; San Miguel et al., 2004).

In 1997, the waste management policy changed. A new water recycling system was introduced in order to minimize the environmental impact of this activity on the river system. In nowadays, the water follows a closed circuit avoiding any transfer of

radionuclides into the environment. In this way, riverine water is used for pumping and, following gypsum decantation, the same water mass is used in order to continue the waste transportation process. As a consequence of the new waste policy, a self-cleaning process has taken place in this estuary because a systematic and continuous decrease in activities was found in the water column and in bed sediments (Absi et al., 2004; Periáñez et al., 2004).

Beside the change in the waste management policy, since the mid 1990's, several restoration works have been developed at the phosphogypsum piles. To do that, different PG piles (not all of them) have been covered with succesive layers of different materials. Both composition, homogeneity and thickness of these covers are different for each sector under restoration. At present, only preliminary works have been focussed in the evaluation of the efficiency of this technique as a possible shield against ionizing radiation (Mas et al, 2001).
The Study area has been divided into four zones according to the state of restoration works in them (Figure 1):

a) Zone 1

The zone 1 (Figure 1) is a 450 Ha sector, and it was the first area submitted to regeneration work. It is calculated that about $12 \cdot 10^6$ Tonnes of PG, including unknown amounts of urban wastes and mining wastes, were released in this sector. Restoration tasks were performed during 1990 by the Andalusia Regional Government in order to minimize both the visual and the environmental impact associated to the different wastes there released. To do that, a soil cover of about 30 cm average thickness and a vegetal coverage were added above the naked PG surface. Furthermore, several tenths of soil hills (1.5 m height) were scattered above the soil cover layer in order to allow small tree species to growth.

b) Zone 2

In the zone 2 (270 Ha, Figure 1), the wastes are being released in nowadays inside the water recirculation system. In this zone, the gypsum stacks has reached 15 m height above the natural ground, and it continues growing following a pyramid shape. As the height

increases, the sides of the pyramid are covered with a soil layer and a vegetal coverage, in order to minimize the visual impact.

c) Zone 3

The zone 3 (180 Ha, Figure 1) is close to zone 2. It is only conformed by PG, without any soil coverage. This sector will be used for future pile up when the zone 2 should be completed.

d) Zone 4

The zone 4 is being submitted to a similar restoration process. More detailed, different kinds of industrial and urban wastes are being added above the PG: in first place, a building debris layer was added; thereafter, different kinds of industrial wastes and finally, a soil layer like that of the zone 1 for different vegetable species can growth on this cover. The total thickness of the coverage (including the three layers: wastes, debris and soil) is more than 1 m. One of the material proposed for covering consists of wastes arising from different industries of the Huelva estuary: in particular those from the painting pigment TiO_2 production industry. This possibility could be negative from the dosimetric point of view as will be shown below.

Furthermore, one of the sectors contained within the PG stacks was contaminated some years ago by the radioactive ashes produced during the Acerinox Steel factory accident in 1998 (http://www.csn.es/descarga/aceri12.html). An industrial ^{137}Cs radioactive source was accidentally melted with iron wastes in the steel factory. These wastes were treated in an purifier plant of the industrial complex of Huelva as usual. Finally, the wastes and a certain amount of these ashes were released in the zone 4 and mixed with the PG. As a consequence of the releases, the Spanish National Wastes Enterprise (ENRESA) sealed the sector and restoration works were developed consisting in a cover with a layer of clay to minimize permeability and migration of radioactive cesium. Finally, different vegetal species was planted in the sector, and a vigilance program was established.

2.2 Sampling of soils, gypsum, sediments and the covering materials

The sampling was carried out according to the very clear division established on the area under study after developing the restoration tasks.

Zone 1

PG and soil samples were taken from nine different locations at the zone 1 (Figure 1). Two PG samples were taken at each sampling location: the first one was taken at 30 cm depth (i.e., just below the soil, in the upper layer of PG), the second one was collected at 60 cm depth. Furthermore, a surface soil sample was also recorded from the same location.

Zone 2

Seven samples of surface soil and the PG just below the soil were collected from this zone (Figure 1).

Zone 3

This zone was divided in four sub-zones and a core ("T") was recorded from each one at different depths: a surface gypsum sample ("A") and a deep sample (30-60 cm depth) ("B") (Figure 1). In the proximities of these points four surface gypsum samples were also collected.

Zone 4

From this zone, two PG samples from the still naked PG surface were collected (Figure 1). The corresponding sampling points were covered as previously described some time after the sampling. Furthermore, debris and industrial wastes samples from the inner thick coverage were recorded.

Also, in order to evaluate the possible radiological impact for workers and the degree of dispersion of radioactive cesium, four additional surface samples were recorded from the sector where the ashes contaminated by ^{137}Cs were released (samples CZ1 to CZ4, Figure 1).

After collection, the samples were transported to our laboratory. The water content was determined and removed by the constant weight method at 65ºC. All the samples were reduced by milling to a grain size less than 0.2 mm. Note that the PG composition is mainly $CaSO_4 \cdot 2H_2O$, so the dehydration of PG molecules is avoided by drying the sample at 65 °C.

2.3 Radionuclide activity measurements

Gamma-ray Spectrometry

Gamma-ray measurements were performed using an XtRa coaxial Ge detector (Canberra), with 38% relative efficiency and resolution (FWHM) of 0.95 keV at the 122 keV line of ^{57}Co and 1.9 keV at the 1333 keV line of ^{60}Co. The detector was attached to a conventional electronic chain, including a multichannel analyser, and was shielded with Fe 15 cm thick.

We developed an original efficiency calibration procedure in the energy range of 150-1800 keV (Pérez-Moreno et al., 2002). Radium-226 activities were determined via the 352 keV emission of ^{214}Pb. Both nuclides were in secular equilibrium since counting was done at least one month after filling and sealing the sample container. Radium-228 determination were carried out by the emission of 911 keV of ^{228}Ac, which is in secular equilibrium with its precursor. Cesium-137 activities were determined by 662 keV gamma photons. Thorium-228 has been determined by the 583 keV photons of ^{208}Tl taking into account the branch ratio in the decay scheme of these radionuclides. On the other hand, ^{210}Pb activities have been also determined from the same measurement by using an independent efficiency calibration developed specifically for the photons of 46.5 keV emitted by this radionuclide (San Miguel et al., 2002).

Alpha spectrometry

U-isotopes mass activities were determined in the samples by alpha-particle spectrometry. For the determination of U-isotopes mass activities by alpha-particle spectrometry in the samples, a sequential well-stablished radiochemical method to the samples was applied

(Holm and Fukai, 1977). In this method the U-isotopes are electrodeposited onto stainless steel planchets (Hallstadius, 1984). Typical recovery yields of 60-80% were obtained.

The U planchets were measured using an EG&G Ortec alpha spectrometry system with ion-implanted silicon detectors. Counting times ranged from two days to one week, depending on the activity concentrations and the recovery obtained in the chemical separation. The alpha spectrometry system was specially devoted to the measurement of low-level activities.

2.4 Dose rate measurement

External dose rates due to photons coming from the soil/PG system were directly measured using a dose rate monitor Berthold Umo LB123 coupled to an environmental probe LB1236. This monitor works in a proportional regime, being sensitive within the energy range 30-2000 keV, with an effective dose rate sensitivity over the background from 50 nSv h^{-1} up to 10 mSv h^{-1}. The cosmic rays and electronic noise contribution to the background of the counting system were about 0.28 mSv y^{-1} and 0.25 mSv y^{-1}, respectively. The measurements have been corrected for the background. **The measurements were carried out 1 m above the surface of the ground/PG pile. From every sampling site, five measurements (1-minute each) were recorded in order to achieve an adequate statistics.**

3. Results and discussion

3.1. Radioactivity of soil and phosphogypsum.

3.1.1 Zone 1

The results for soil and PG samples in the Zone 1 are shown in Table 1. It can be seen that the radioactive concentrations in soils samples of the nuclides from the ^{238}U and ^{232}Th series are quite close, and even slightly less, than for the worldwide average soil concentration according to United Nations (UNSCEAR, 2000). Furthermore, all the

radionuclides are in secular equilibrium. This result shows the natural, unperturbed origin of the soils used in the coverage layer.

For every soil sample, the ^{137}Cs activity remained below the detection limit (0.4 Bq kg^{-1}). This value is in disagreement with previous assays for this nuclide in surface natural soils of the same region (Vaca et al., 2001). This means that the soil used for the vegetal cover has not been exposed to the atmospheric fallout during the past 40 years. Actually, they were previously extracted from a quarrel-mining facility close to this region. This assay was confirmed by the activity ratio $^{210}Pb/^{226}Ra$, which was never more than 1.0. Hence, these soils never suffered atmospheric lead input, according to the information provided by the analysis of ^{137}Cs activities.

Concerning the phosphogypsum samples, no secular equilibrium between the different radionuclides has been found, as expected. The greater mass activities were found for ^{226}Ra and ^{210}Pb, a fact which is in agreement with previous works (Guimond and Hardin, 1989; Rutherford et al., 1994; Hull and Burnett et al., 1996; Bolívar et al. 2000). This is due to the similar chemical behaviour of Ra and Pb, which trend to co-precipitate with the gypsum matrix. The ^{210}Pb mass activities are about 30% less than ^{226}Ra mass activities, as their precipitation trends are slightly different (Bolívar et al., 1996). On the contrary, mass activities for U isotopes are less than for ^{210}Pb, as they trend to be accumulated with the phosphoric acid as a consequence of the high solubility of the Uranyl ion (UO_2^{++}).

The high ^{226}Ra mass activities are in agreement with previous studies on this area (EGMASA, 1996; Cancio et al., 1998). On the other hand the mass activities associated to the ^{232}Th-Series nuclides are about half and ten times less, respectively than those values in typical soils. This fact is a consequence of their low contents in the phosphate rock. In all the PG samples analysed in this zone, the mass activities of ^{137}Cs were below the minimum detectable specific activity 1 Bq kg^{-1} while the ^{40}K ones were in the 10-30 Bq kg^{-1} range.

According to this analysis, bearing in mind the production of ^{222}Rn by the ^{226}Ra decay, and due to its high radiotoxicity, it results clear that ^{226}Ra becomes the more important factor to be controlled in the phosphogypsum stacks. As a consequence, it seems peremptory to

begin studies on the lixiviation degree of Ra atoms from the phosphogypsum stacks to the close environment as a consequence of the action of natural agents, such as meteorological factors, tidal waters and naturally occurring percolation effects.

3.1.2 Zone 2

The results for soil and PG samples in the zone 2 are shown in Table 2. The results for PG samples are quite similar to those found in Zone 1, and therefore only the major differences will be discussed here.

The ^{210}Pb mass activities in this zone present the greatest values of the different analysed zones (520 ± 60 Bqkg^{-1}). Two hypotheses can be considered in order to explain this fact: 1) the changes introduced in 1997 in the wastes management policies and 2) the different exposition time of PG to the lixiviation process, depending on the zone under study. It is well known that Pb shows a higher lixiviation degree than Ra (Aguado, 2003). Among all the phosphogypsum analysed in this work, those of the Zone 2 have had less exposure to environment. In this way, the phosphogypsum at this zone has suffered less lixiviation processes, and as consequence, it can be expected the greatest ^{210}Pb mass activities in this zone.

Concerning the soil samples, the mass activities and activitiy ratios are quite similar to those of Zone 1. However, a very interesting difference appears: the ^{137}Cs mass activity values are clearly higher than detection limits. This fact indicates that these soils were exposed to atmospheric fallout. Then, besides the previously mentioned fact, it can be concluded that these soils are different in origin from those used for Zone 1.

3.1.3 Zone 3

The results for the phosphogypsum core and surface phosphogypsum samples in the zone 3 are shown in Table 3. As expected, the radionuclide concentrations are quite scattered along surface axis, with large variations depending on the sampling point. This fact is a consequence of both changes in the industrial process and the phosphate rock origin, which affects the ^{238}U-series radionuclide concentrations (Rutherford et al., 1996).

The mass activities were usually higher for samples collected at higher depth than for surface phosphogypsum. This trend is particularly clear for uranium isotopes. This fact is in agreement with the expected higher solubility of U atoms, which produces the highest mobility among all the elements here analysed including radionuclide migration mechanisms. In both core and surface phosphogypsum samples, the values of ^{137}Cs and ^{40}K are below the minimum detectable specific activity, 1 and 13 Bq kg^{-1}, respectively.

3.1.4 Zone 4

The results for soil and PG samples in the zone 2 are shown in Table 4. As the results for phosphogypsum samples were quite similar to the previous results, no further comment will be developed here. However, a general comment regarding the U contents can be added. The ^{238}U concentrations are higher in samples collected at Zone 2, i.e., the unique zone which is actually active. This fact can be related with the enhanced uranium solubility in seawater against its solubility in river water, according to their different ion strengths. As the old phosphogypsum transport system used seawater, the higher uranium solubility produced a higher concentration in water, and a minor concentration in phosphogypsum. This result is also in agreement with previous forced lixiviation experiments (Aguado, 2003).

As above mentioned, the samples CZ-1 to CZ-4 were collected from the sector where the ashes contaminated with ^{137}Cs were released. At the sampling time, the radioactive source was sealed by the Spanish National Wastes Enterprise (ENRESA); so only an assay on the possible radionuclide dispersion was performed. It is possible to inferred that the ^{137}Cs dispersion has been extremely small up to the date in the sector corresponding to CZ1 and CZ2 samples. Only small amounts (around 30 Bq kg^{-1}) were detected in a sample. This value is approximately five times higher than fallout values for typical soils of this region (Vaca et al., 2001). The radiological concern is, at this time, negligible (see next section for details). However, this finding poses a special attention on the future needs for controlling this sector. It is strongly recommended to develop more exhaustive sampling in the surroundings of the CZ3 and CZ4 zone in order to delimitate the degree of ^{137}Cs dispersion. This recommendation is also based on the fact that higher ^{137}Cs dispersion was

found at this zone, where mass activities higher than 200 Bq kg^{-1} were found. However, due to the isolated character of this contribution, it can be expected that the radiological effect may be negligible.

Regarding the corresponding soils, the results are in agreement with the character of unperturbed systems, as secular equilibrium between the different radionuclides was found. According to the ^{40}K contents, the total potassium content can be established in the range of 1.4%.

An additional general comment can be established regarding the cover system of this sector. It can be seen that the industrial wastes show radionuclide concentrations higher than other materials used in the coverage system. Special attention must be posed on the first layer used in this coverage system, as Th and Ra isotope concentrations are very high inside the TiO_2 production wastes. These wastes derive from the mud produced in the lixiviation of ilmenite for the production of TiO_2. It seems that during the industrial process, there is a fractionation of the radioactivity contained onto the mineral.

3.2 Dosimetric assay

The dose rates received at the PG piles or close regions due to gamma-ray photons in the soil must be compared to the natural soil background values. Such values have been previously established in the range of 0.40 mSv y^{-1} (Mas et al., 2001). The values of the external annual effective dose obtained from direct monitoring in the different sectors are shown in Table 5. **In what follows, results indicate the external annual effective dose assuming an exposition time of a whole year (i.e., 8760 h). These results should be corrected by the corresponding occupational factor, as it is indicated below.**

As can be seen from this table, the values recorded in zone 1 are in the same range of the natural background, with an average of 0.31 ± 0.09 mSv y^{-1}. This was due to the

attenuation effect associated to the presence of the soil cover layer and the low content of radionuclides in this sector, which leads to a low dosimetric contribution.

Dosimetric readings from zone 2 reflects values up to eight times higher than natural background, with an average of 1.6 ± 0.4 mSv y^{-1}. The source of this increment is the high radionuclide concentrations in the phosphogypsum and the absence of a covering layer in this sector. It is worth noting that these values are lower than previous data collected at the same sector: 2.5 ± 0.5 mSv y^{-1} (EGMASA, 1996) and 2.15 ± 0.27 mSv y^{-1} (Cancio et al., 1998). This fact was due to the introduction of the new water circulation system. As a large proportion of the previously uncovered surface is covered actually with the circulation water, the water acts as a shield against radiation coming from underlying phosphogypsum. This fact was reflected in zone 3, where the shield of water does not exist. As a consequence, an average of 2.3 ± 0.5 mSvy^{-1} was recorded at sector 3. The high positional dispersion reflects the highly variable radionuclide concentrations described in the previous section.

Concerning the zone 4, the values are quite close to the previously mentioned background values, especially at those points where a vegetable cover layer has been disposed. The dispersion of data in this case is very small (about 6%). This fact indicate that the radionuclide concentrations are homogeneous within the material used for the cover layer.

The values obtained have to be corrected for the corresponding occupational factor. In this case and assuming the worst case, i.e., a working time of 8 hours-a-day throughout the whole year, the occupational factor should be 1/3. In this way, it results clear that all the corresponding doses are below the limits **for population** according to the European regulation (1 mSv y^{-1}), even assuming that workers spend the whole 8 h-working day above the phosphogypsum piles. It is worth noting that this is the most unfavourable situation.

According to these data, it can be deduced that the new restoration works are being successful from the point of view of the external dose rate reduction, although the active

piles are representing still a problem. Nevertheless, this problem could be reduced if a strong control on the presence of workers above these piles is established in order to minimize the workers occupational exposure.

Furthermore, an alternative for the covering system of sector 4 has been proposed recently. The proposed material consists of wastes of TiO_2 production industry for painting pigments. This industry uses the so-called ilmenite rock as a raw material. It is a well known fact that this rock contains very high amounts of naturally occurring ^{232}Th (Collier et al., 2001), which is the parent nuclide of the thorium series. However, there are not any kind of radiological control or previous analysis of this industrial process (Betti et al., 2004), so a special care on the radiological implications associated to the management of their wastes seems peremptory.

In order to test the radiological implication of this practice, a single dosimetric model has been applied to specific geometries of the soil/coverage system. This model offers the following advantages: 1) it is very easy to apply provided that several conditions can be assumed, and 2) it has been previously tested for similar systems, showing a good agreement against true monitoring (Bolívar et al., 1998).

This model allows the calculation of the external dose rate due to photons coming from soil knowing the mass activities of radionuclides in soil and phosphogypsum. In this way, the dosimetric contribution from each layer in the system (i.e., soil and each layer of the coverage) can be estimated. The hypotheses for application of this model are the following:

1. The surface (or volume) containing the photon emitter radionuclides have infinite extension. Of course, this is not true but due to the extension of surfaces implicated in this work, the geometrical corrections to be established are negligible (Bolívar et al., 1998).

2. It is assumed that concentrations of radionuclides in the system is homogeneous both along vertical and surface axis. Once again, this is not true according to the results

developed in the next section; however, we considered average values in this work in order to correct this lack of homogeneity. This could be a possible reason for discrepancies found between the values predicted by the model and the experimental results. An additional point is the existence of vertical differences for radionuclide concentrations, i.e. the presence of very different layers having very different radionuclide contents (e.g., phosphogypsum, inert material, building debris and soil layer). Hence, we adapted the model in order to correct this point, by dividing the whole block in different layers with different radionuclide contents. Each of these layers was assumed to have homogeneous radionuclide contents.

Details of the dosimetric model were explained elsewhere (Mas et al., 2001); therefore only applications will be shown here. Three different phosphogypsum/coverage arrangements have been considered:

1) *Geometry 1*: Naked phosphogypsum has been considered. The average value of mass activities calculated from samples 4-1 and 4-2 has been used as input of the model.

2) *Geometry 2*: A block of phosphogypsum has been assumed to be covered using a homogeneous layer of IP material (industrial wastes from the TiO2 industrial production process). In this way, we expect to show if this proposed practice could be negative from the dosimetric point of view. IP layer has been assumed to be 50 cm thick.

3) *Geometry 3*: Following a downward address, it consists of: a) a soil layer containing radionuclides according to average values of CZ1, CZ2, CZ3 and CZ4 samples, 50 cm thick; b) a layer containing IP material (industrial wastes from the TiO_2 industrial production process), being the mass activities the same than in the case previously studied and having 50 cm thick; and c) a block of PG. However, the dosimetric contribution from this layer is negligible because gamma photons emitted from the PG block are attenuated by the layers superimposed above it, with a whole thickness of 100 cm, according to the calculations performed by Mas et al. (2001).
The external absorbed dose values obtained through these calculations for the three geometries are shown in Table 6.

For the geometry 1, the results obtained are quite similar to those previously obtained at zones 2 and 3, as expected according to the lack of coverage. According to the results obtained for the geometry 2, there is an increase in the calculated external annual absorbed dose of about 16% against that produced by naked phosphogypsum. Hence, this practice would introduce an increase on dose rates by a 7-factor against the dose rates produced by natural soils of this region. This fact allows to conclude that such practice would be extremely negative from the dosimetric point of view. It can be also concluded that almost a 66% of the total predicted dose rate is related to the ^{232}Th-series radionuclides. On the contrary, these radionuclides are contributing with only 3% of total external dose for studied geometry 1, due to their very low activities in PG. Finally, results from geometry 3 show that a natural, low radionuclide contents layer should be enough to reduce the external dose up to a low value, quite close from that obtained for regular soils. It is worth noting that this prediction is quite close from data obtained experimentally at zone 4.

4. Conclusions and general remarks

In this work, the effects of the remediation tasks developed in a waste disposal site from a NORM industry have been evaluated. According to the dosimetric data presented, it can be deduced that the new restoration works are being successful from the point of view of the external dose rate reduction. Nevertheless, the active piles still represent a radiological concern that could be reduced by establishing a control on the presence of workers above these piles.

It is strongly recommended to develop more exhaustive sampling in the surroundings of the sector where the ashes contaminated by ^{137}Cs were released, especially in the surroundings of the CZ3 and CZ4 collection points to delimitate the degree of ^{137}Cs dispersion.

It was also detected that the use of certain industrial wastes as covering material in the remediation tasks would be extremely negative from the dosimetric point of view leading to external dose rate increases about 7 times higher than those produced by regular soils of this region. This fact makes recommendable a radiological control of the different industrial wastes that could be proposed as a cover in these kinds of restoration works.

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FIGURE CAPTIONS

Figure 1.-. Location map of the phosphogypsum piles close to Huelva town (SW of Spain).

TABLE CAPTIONS

Table 1.-. Radionuclide concentrations (Bq kg^{-1}) found within soil (Table 1.a) and phosphogypsum samples (Table 1.b) collected at zone 1: G1 and G2 indicate phosphogypsum at 30 cm and 60 depth respectively. (*) This sample was corresponding to industrial wastes, and not to soil.

Table 2.- Radionuclide concentrations (Bq kg^{-1}) found within soil (Table 2.a) and phosphogypsum samples (Table 2.b) at zone 2.

Table 3.- Radionuclide concentrations (Bq kg^{-1}) found at Sector 3: in phosphogypsum cores (Table 3.a): codes “A” and “B” indicate surface (0-20 cm) and deep (50-70 cm) sections, respectively; and in surface phosphogypsum samples (Table 3.b).

Table 4.- Radionuclide concentrations (Bq kg^{-1}) at sector 4. CZ: Soil samples from the surroundings of the Acerinox incident ashes disposal site. YR: Industrial wastes. IP: Industrial wastes from the TiO2 industrial production process. RDC: Building debris. 4-1 and 4-2 are phosphogypsum samples from not yet covered sector.

Table 5.- External annual effective dose (mSv y^{-1}) due to photons arriving from soil/phosphogypsum system.

Table 6.- External annual absorbed dose ($mGyy^{-1}$) due to gamma photons arising either from the phosphogypsum or the phosphogypsum/cover system according to the dosimetric model and considering three different system arrangements.

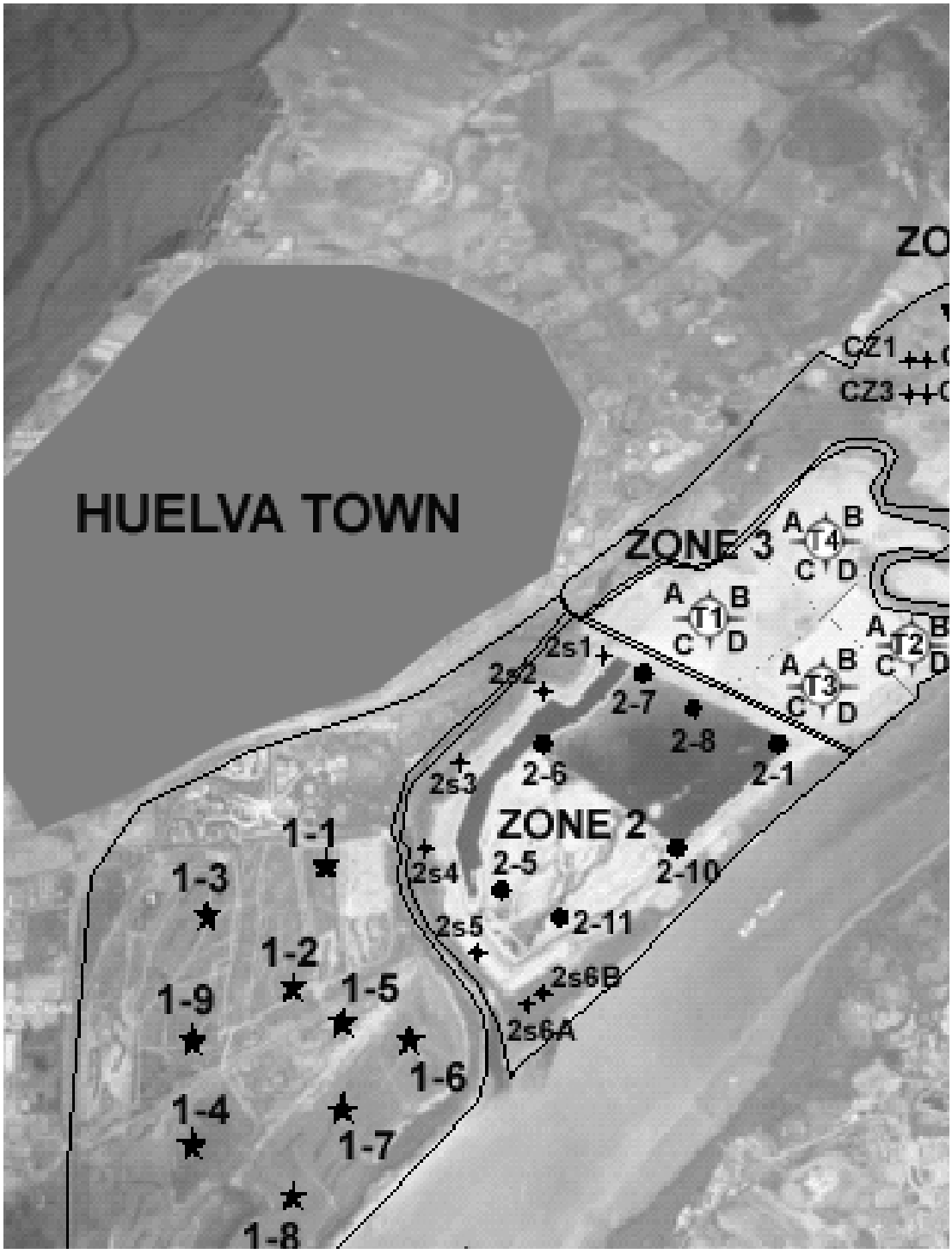
HUELVA TOWN
ZONE 3
ZONE 2
CZ1
CZ3
T1
T2
T3
T4
A
B
C
D
2s1
2s2
2s3
2s4
2s5
2s6A
2s6B
2-1
2-5
2-6
2-7
2-8
2-10
2-11
1-1
1-2
1-3
1-4
1-5
1-6
1-7
1-8
1-9

Figure 1

Sample	^{226}Ra	^{228}Ra	^{40}K	^{210}Pb	^{234,238}U	^{228}Th
1-1-S	11.8 ± 0.8	18.4 ± 1.3	238 ± 13	13.7 ± 1.3	8.8 ± 1.4	17.4 ± 1.0
1-2-S	12.5 ± 0.9	21.2 ± 1.5	226 ± 12	12.4 ± 2.4	19 ± 3	22.7 ± 1.4
1-3-S	23.0 ± 1.5	22.7 ± 1.7	290 ± 16	16.5 ± 2.1	22 ± 3	21.8 ± 1.4
1-4-S	27.3 ± 1.6	22.9 ± 1.5	370 ± 19	25.2 ± 1.8	22.1 ± 2.5	21.5 ± 1.2
1-5-S	33.3 ± 2.0	22.0 ± 1.5	394 ± 20	38.2 ± 2.3	26 ± 3	20.8 ± 1.2
1-5-S2 (*)	13.6 ± 0.9	55.8 ± 3.5	54 ± 4	9.1 ± 1.1	9.8 ± 1.5	48 ± 3
1-6-S	23.6 ± 1.4	26.9 ± 1.8	265 ± 14	27.2 ± 1.8	19.6 ± 2.3	23.0 ± 1.3
1-7-S	20.0 ± 1.2	24.4 ± 1.6	282 ± 15	24.8 ± 1.8	18.6 ± 2.2	21.5 ± 1.2
1-8-S	15.1 ± 1.0	18.6 ± 1.3	299 ± 16	17.3 ± 1.7	10.9 ± 1.8	17.8 ± 1.1
1-9-S	30.4 ± 1.8	21.2 ± 1.4	253 ± 13	38.6 ± 2.1	37 ± 4	19.3 ± 1.1
Average	**21 ± 7**	**22 ± 3**	**290 ± 60**	**24 ± 9**	**20 ± 8**	**21 ± 2**

Table 1.a

Sample	^{226}Ra	^{228}Ra	^{210}Pb	^{234,238}U	^{228}Th
1-1-G1	590 ± 40	7.2 ± 1.1	450 ± 20	24 ± 5	6.3 ± 0.8
1-1-G2	480 ± 30	8.3 ± 1.1	434 ± 20	90 ± 9	5.8 ± 0.8
1-2-G1	650 ± 40	3.8 ± 1.1	439 ± 20	72 ± 8	5.8 ± 0.8
1-2-G2	620 ± 40	7.6 ± 1.3	447 ± 21	68 ± 8	5.6 ± 0.9
1-3-G1	580 ± 30	10.0 ± 1.4	450 ± 21	78 ± 9	9.3 ± 1.0
1-3-G2	570 ± 30	8.1 ± 1.3	437 ± 20	113 ± 11	23.1 ± 1.5
1-6-G1	730 ± 40	18.0 ± 1.7	471 ± 22	133 ± 13	18.3 ± 1.3
1-6-G2	770 ± 50	18.3 ± 1.8	386 ± 18	105 ± 11	21.1 ± 1.4
1-7-G1	650 ± 40	12.9 ± 1.4	440 ± 20	199 ± 19	12.2 ± 1.1
1-7-G2	660 ± 40	13.7 ± 1.8	399 ± 19	31 ± 5	28.8 ± 1.9
1-8-G1	600 ± 40	8.3 ± 1.4	408 ± 19	74 ± 8	16.1 ± 1.2
1-8-G2	1110 ± 70	16.9 ± 1.9	482 ± 22	218 ± 21	18.3 ± 1.5
1-9-G1	560 ± 30	8.9 ± 1.3	348 ± 16	142 ± 14	9.4 ± 1.0
1-9-G2	610 ± 40	8.1 ± 1.2	528 ± 24	67 ± 8	8.1 ± 0.9
Average	**620 ± 70**	**11 ± 4**	**440 ± 40**	**100 ± 60**	**13 ± 7**

Table 1.b

Sample	^{226}Ra	^{228}Ra	^{137}Cs	^{40}K	^{210}Pb	^{234,238}U	^{228}Th
2-S1	23.3 ± 1.4	28.5 ± 1.8	< 0.28	587 ± 30	19.4 ± 1.7	20.2 ± 2.4	26.8 ± 1.5
2-S2	14.3 ± 0.9	17.6 ± 1.2	0.25±0.08	239 ± 12	8.7 ± 1.2	8.6 ± 1.4	16.2 ± 0.9
2-S3	31.8 ± 1.9	31.8 ± 1.9	0.39±0.10	304 ± 16	26.8 ± 1.9	24 ± 3	35.5 ± 2.0
2-S4	27.3 ± 1.7	39 ± 3	2.2 ± 0.2	247 ± 14	24 ± 3	25 ± 4	35.6 ± 2.1
2-S5	22.1 ± 1.4	27.1 ± 1.9	< 0.50	380 ± 20	21.6 ± 2.4	16 ± 3	25.3 ± 1.5
2-S6-A	22.3 ± 1.4	32.3 ± 2.2	0.7 ± 0.2	401 ± 21	18 ± 3	18 ± 3	30.2 ± 1.7
2-S6-B	21.6 ± 1.3	22.6 ± 1.5	< 0.31	360 ± 19	17.3 ± 1.6	17.3 ± 2.1	20.9 ± 1.2
Average	**23 ± 5**	**28 ± 6**	**< 0.7**	**360 ± 120**	**20 ± 5**	**19 ± 5**	**27 ± 7**

Table 2.a

Sample	^{226}Ra	^{228}Ra	^{210}Pb	^{234,238}U	^{228}Th
2-G5	650 ± 40	10.4 ± 1.1	472 ± 22	158 ± 15	11.1 ± 0.9
2-G6	570 ± 30	5.4 ± 1.2	580 ± 30	133 ± 13	6.7 ± 0.9
2- G7	688 ± 40	10.8 ± 1.3	541 ± 25	72 ± 8	7.8 ± 0.9
2- G8	710 ± 40	7.6 ± 1.4	460 ± 21	510 ± 50	10.3 ± 1.1
2- G9	710 ± 40	7.2 ± 1.3	590 ± 30	82 ± 9	7.9 ± 0.9
2- G10	670 ± 40	10.0 ± 1.3	518 ± 24	173 ± 17	7.9 ± 0.9
2- G11	720 ± 40	10.0 ± 1.0	451 ± 20	427 ± 40	6.1 ± 0.7
Average	**670 ± 50**	**9 ± 2**	**520 ± 60**	**220 ± 170**	**8.2 ± 1.8**

Table 2.b

Sample	^{226}Ra	^{228}Ra	^{210}Pb	^{234,238}U	^{228}Th
3T1-A	490 ± 30	9.7 ± 1.3	414 ± 19	35 ± 5	9.6 ± 1.0
3T1-B	600 ± 30	9.8 ± 0.8	544 ± 25	106 ± 10	8.3 ± 0.6
3T2-A	560 ± 30	8.3 ± 1.2	412 ± 19	75 ± 8	6.0 ± 0.8
3T2-B	770 ± 50	8.9 ± 1.3	522 ± 24	108 ± 11	10.3 ± 1.0
3T3-A	570 ± 30	10.5 ± 1.3	545 ± 25	140 ± 14	18.4 ± 1.3
3T3-B	470 ± 30	8 ± 3	441 ± 21	117 ± 12	7.8 ± 2.0
3T4-A	740 ± 40	7.1 ± 1.2	560 ± 30	96 ± 10	7.1 ± 0.9
3T4-B	790 ± 50	12.8 ± 1.6	520 ± 24	141 ± 14	13.5 ± 1.2
Average	**620 ± 130**	**9.4 ± 1.8**	**500 ± 60**	**100 ± 30**	**10 ± 4**

Table 3.a

Sample	^{226}Ra	^{228}Ra	^{210}Pb	^{234,238}U	^{228}Th
3-1A	300 ± 18	9.4 ± 1.2	278 ± 13	115 ± 12	9.0 ± 0.8
3-1B	428 ± 25	8.7 ± 1.1	482 ± 22	53 ± 6	8.3 ± 0.9
3-1C	520 ± 30	11.2 ± 1.3	538 ± 25	77 ± 9	9.2 ± 0.9
3-1D	393 ± 23	11.2 ± 1.2	360 ± 17	91 ± 9	9.3 ± 0.9
3-2A	820 ± 50	12.9 ± 1.4	610 ± 30	120 ± 13	9.8 ± 1.0
3-2B	640 ± 40	13.2 ± 1.5	360 ± 17	103 ± 11	12.1 ± 1.1
3-2C	610 ± 40	8.7 ± 1.2	474 ± 22	88 ± 9	7.2 ± 0.9
3-2D	(*)	12.5 ± 1.6	471 ± 22	(*)	11 ± 3
3-3A	760 ± 40	10.2 ± 1.7	570 ± 27	106 ± 12	14.7 ± 1.4
3-3B	530 ± 30	8.2 ± 1.2	560 ± 30	90 ± 10	7.8 ± 0.8
3-3C	460 ± 30	6.1 ± 0.8	496 ± 23	84 ± 8	6.3 ± 0.6
3-3D	540 ± 30	9.5 ± 1.3	461 ± 21	55 ± 10	7.9 ± 0.9
3-4A	590 ± 30	13 ± 4	451 ± 21	45 ± 6	7.3 ± 0.9
3-4B	440 ± 30	4.0 ± 0.7	456 ± 21	71 ± 7	2.9 ± 0.5
3-4C	630 ± 40	4.8 ± 1.2	424 ± 20	69 ± 8	6.6 ± 0.9
3-4D	440 ± 30	6.2 ± 1.0	324 ± 15	56 ± 6	4.1 ± 0.7
Average	**568 ± 137**	**9 ± 3**	**470 ± 80**	**90 ± 30**	**8 ± 3**

Table 3.b

Sample	^{226}Ra	^{228}Ra	^{137}Cs	^{40}K	^{210}Pb	^{234,238}U	^{228}Th
CZ1	26.1 ± 1.6	28.4 ± 2.0	< 0.53	445 ± 24	20 ± 3	20 ± 3	25.9 ± 1.6
CZ2	23.0 ± 1.4	27.3 ± 1.9	30.2 ± 1.6	397 ± 21	20 ± 3	22 ± 3	24.4 ± 1.5
CZ3	23.6 ± 1.5	32.1 ± 2.2	235 ± 12	461 ± 24	35 ± 3	23 ± 4	27.5 ± 2.2
CZ4	26.5 ± 1.6	30.4 ± 2.0	139 ± 7	510 ± 30	23.2 ± 2.3	23.2 ± 2.3	26.8 ± 1.5
IP	233 ± 14	630 ± 40	< 1.5	258 ± 15	65.2 ± 4.1	21 ± 4	215 ± 12
YR	10.8 ± 0.9	41 ± 3	< 0.85	10 ± 3	7.8 ± 1.5	5.6 ± 1.7	77 ± 4
RDC	45 ± 3	29.2 ± 2.0	1.4 ± 0.2	244 ± 14	23.2 ± 2.4	19 ± 3	26.0 ± 1.6
4–1	630 ± 40	15.7 ± 1.6	< 0.08	13 ± 4	442 ± 21	18 ± 4	12 ± 3
4–2	520 ± 30	10.5 ± 1.3	< 0.07	< 9.8	405 ± 19	27 ± 4	14.8 ± 1.1

Table 4

Zone	N	Average (mSv y^{-1})	Range (mSv y^{-1})
1	9	0.31 ± 0.09	0.15-0.46
2	17	1.6 ± 0.4	0.64 – 2.48
3	4	2.3 ± 0.5	1.90 – 3.12
4	6	0.49 ± 0.03	0.43 – 0.57

Table 5

PG/cover arrangement	Geometry 1	Geometry 2	Geometry 3
^{238}U-series	2.36	0.943	0.130
^{232}Th-series	$7.26 \cdot 10^{-2}$	1.80	0.210
^{235}U-series	$1.17 \cdot 10^{-3}$	$1.64 \cdot 10^{-3}$	$1.93 \cdot 10^{-3}$
^{40}K	$4.08 \cdot 10^{-3}$	$8.67 \cdot 10^{-2}$	$1.56 \cdot 10^{-2}$
Total	2.44	2.83	0.358

Table 6