Radiation Protection Dosimetry
Vol. 76, No. 3, pp. 185–189 (1998)
Nuclear Technology Publishing

TECHNICAL NOTE

RADIOACTIVITY OF PHOSPHOGYPSUM IN THE SOUTH-WEST OF SPAIN

J. P. Bolívar†, R. García-Tenorio‡ and J. Mas†
†Departamento de Física Aplicada, E.P.S. La Rabida
Universidad de Huelva, 21819-Palos de la Fra. Huelva, Spain
‡Departamento de Física Aplicada, E.T.S. Arquitectura
Avda Reina Mercedes s/n, 41012-Sevilla, Spain

Received June 24 1997, Amended November 25 1997, Accepted December 12 1997

Abstract — Phosphogypsum is the by-product of producing phosphoric acid by reacting phosphate rock with sulphuric acid. In the south-west of Spain, and near the town of Huelva, there is a big industrial complex with some factories devoted to the production of phosphoric acid, which produce annually 3×10^6 metric tonnes of phosphogypsum. Of this amount 80% is stored in nearby sites named 'gyp-stacks'. The phosphate rock treated in these factories for the production of phosphoric acid has ^{238}U activities between 1000 and 1600 Bq.kg^{-1}, being their daughters in approximately secular equilibrium. A fraction of these radionuclides, and in different proportion, goes with the phosphogypsum. The radionuclide activity concentrations in various phosphogypsum samples collected at different places in the gyp-stacks are given, and an average dose rate in air due to gamma rays at a point 1 m above these areas is also determined.

INTRODUCTION

In the south-west of Spain, near the town of Huelva, and just in the estuary formed by the confluence of the Odiel and Tinto river mouths, there is a big industrial complex with several factories devoted to the production of phosphoric acid from phosphatic rocks. These sedimentary rocks come from different places in the world (Morocco, Senegal and Togo), and contain about 1000–1600 Bq.kg^{-1} of ^{238}U, with its daughters (^{230}Th, ^{226}Ra, ^{210}Po, …) in near secular equilibrium[1].

This equilibrium is disrupted when the phosphatic rock is treated with sulphuric acid to produce phosphoric acid by the so-called 'wet acid method'[2]. In this process, in addition to the phosphoric acid, dy-hidrated calcium sulphate is generated as a by-product, commonly known as phosphogypsum. About 3×10^6 metric tonnes of phosphogypsum are annually produced in the factories, 20% of this amount being directly released into the Odiel river, while the remaining 80% is stored in very extensive zones, named gyp-stacks, placed near the factories.

From previous works it is known that phosphogypsum contains the same radionuclides, but in different proportions, as the phosphate rock[2,3], and so the former has the potential to pollute the environment radiologically[4–6]. In this work, the concentrations of several radionuclides from the U-series (^{238}U, ^{234}U,^{226}Ra and ^{210}Po) have been determined in samples of phosphogypsum collected in different places of the gyp-stacks, and at different depths, as a first step to study some of the principal radiological concerns related to the phosphogypsum storage: the possible contamination of groundwater with ^{226}Ra[7] and/or ^{210}Po[8]. Secondly, and based on the information obtained, an average absorbed dose rate in air at 1 m above these zones has been calculated, as a partial evaluation of their radiological hazard. This calculated dose rate is compared with measurements carried out using an environmental dose rate meter at different representative points of the phosphogypsum piles.

MATERIAL AND METHODS

Collection

The samples of phosphogypsum were collected from some gyp-stacks (covering 4.5×10^6 m^2) placed nearby the factories. A total of seven points was chosen corresponding to gyp-stacks of different ages depending on their formation. In every point two samples of about 1 to 2 kg were collected, one corresponding to the upper 10–20 cm, and the other one at a depth >50 cm. The filling of these gyp-stacks was done over long periods of time, and at the same time phosphate rocks of very different origins have been treated in these factories. With this sampling strategy, the inhomogeneity of the radionuclides distribution can be studied horizontally and vertically over the wide area of the gyp-stacks.

The samples, after collection, were dried and sifted as a preliminary step in radionuclide determination.

In situ measurements

An environmental dose rate meter equiped with a high pressure ionisation chamber was used to measure experimentally the dose rates due to the gamma rays emitted by the material of the phosphogypsum piles. The survey meter readings were taken at 1 m above ground and in 15 locations distributed homogeneously

in the gyp-stacks. At each location at least five readings were recorded, and the average absorbed dose rate calculated, subtracting a background value due to the sensitivy of the system to cosmic radiation and its electronic noise.

Radionuclide determination

Concentrations of U isotopes, ^{210}Po , ^{226}Ra, ^{228}Ra and ^{40}K have been determined in the different phosphogypsum samples. U isotopes and ^{210}Po were determined by alpha particle spectrometry, while the rest were measured by gamma ray spectrometry.

From 0.5 to 1 g of sample, the U isotopes and ^{210}Po were independently isolated applying a liquid–liquid extraction procedure with TBP[5]. Then, the U isotopes were electrodeposited onto stainless steel planchets according to the method of Hastalldius[9], while the polonium was self-deposited onto silver discs in a 2M HCl medium[10]. Chemical recoveries were determined adding, previously to the treatment of the samples, known amounts of ^{208}Po and ^{232}U. The alpha particle spectrometry was performed using four ion-implanted silicon detectors of 350 mm^2 in chambers where a vacuum of ~10^{-1} mm Hg is kept during the measurements. Systematic background runs were made to control possible contamination.

Specific activities of ^{226}Ra, ^{228}Ra and ^{40}K were determined by gamma ray spectrometry, using a HPGe coaxial detector, 14% relative efficiency, and sensitive in the range of 100 keV-2MeV. The measurements were done using a fixed geometry (cylindrical containers of height 5 cm and diameter 6.5 cm), and a special calibration procedure for this geometry was followed. This efficiency calibration takes into account the self-absorption corrections at different energies that must be applied due to variations of densities between the analysed samples and the calibration sample[11].

The ^{226}Ra was determined by taking the photopeak of its daughter nuclide ^{214}Pb at 352 keV, while the ^{228}Ra was measured through the 911 keV gamma emission from its daughter ^{228}Ac, and the ^{40}K by its emission at 1460 keV. To ensure the existence of secular equilibrium between ^{226}Ra and its daughters, the samples were sealed and stored at least for three weeks before the measurements.

All the methods that have been described were validated through the participation in different national and international intercomparison exercises with succesful results as, for example, the IAEA-135 sediment sample.

RESULTS AND DISCUSSION

Radionuclide concentrations

In Table 1 the activity concentrations of the different radionuclides determined in the superficial (S) and deepers (D) phosphogypsum samples are compiled.

From these results, and as was expected, it is possible to deduce the existence of high concentrations of radionuclides belonging to the U series. Conversely, low concentrations of ^{228}Ra (member of the Th series) and ^{40}K were determined, in agreement with previous results, which indicates that their specific activities in the phosphate rocks are either similar or lower than in typical soils[2].

High ^{226}Ra/^{238}U and ^{210}Po/^{238}U activity ratios are found in most samples, showing the tendency of ^{226}Ra and ^{210}Po to go with the phosphogypsum in the wet-acid method, while the uranium generally tends to remain in the phosphoric acid fraction[2].

In fact, based on the fact that the ideal stoichometric phosphatic rock/phosphogypsum mass ratio is 0.59, it can easily be deduced that more than 80% of ^{226}Ra originally present in the phosphate rock remains in the phosphogypsum. In addition, and due to the half-life of ^{210}Po (134.8 days), the tendency of its progenitor, ^{210}Pb, to go with the phosphogypsum fraction can also be deduced, because the ^{210}Po/^{226}Ra activity ratios were near one in the analysed samples, irrespective of the age of phosphogypsum formation and storage.

A clear conclusion from the observed data is also the high dispersion of specific activities for the radionuclides of the U series (as an example, ^{238}U concentrations range from 100 to 600 Bq.kg^{-1}). This fact cannot be considered surprising in view of the different types of minerals treated in the factories, and the possible different effectiveness of the acidulation method, during the years that this process has been carried out. In this sense, it is not surprising that the U isotopes activity concentrations in sample 4D, although it diverges from the general tendency of U fractionation to phosphoric acid: it can be related simply to the incorporation of unreacted phosphate rock and/or oversaturation and re-precipitation of calcium fluorapatite which can occur in the acidulation process, as was established by Hull and Burnett[3].

Another interesting feature can be deduced from the data. In most of the collection points the ^{226}Ra and ^{210}Po activity ratios between the superficial and the deeper samples is lower or equal to one. Even taking into consideration the inhomogeneity of the radionuclide distribution, the general tendency gives evidence of the existence of some ^{226}Ra and ^{210}Po enrichment in the deeper layers. Through a more systematic study in phosphogysum cores, now in progress, an attempt is being made to explain the processes (leaching, migration, incorporation from the waters used to conduct the fresh phosphogypsum to the piles, etc.) that can be responsible for this ^{226}Ra and ^{210}Po enrichment in the deep phosphogypsum samples.

Dosimetric implications

As a way to show the radiological importance of the gyp-stacks, and based on the results previously obtained

about radionuclide concentrations, the average gamma absorbed dose rate, dD/dt, in air at a point 1 m above these zones due to their gamma ray emissions has been calculated.

To do these calculations, we assume the piles to be a semi-infinite volume with radionuclides distributed uniformly[12]. Obviously, the radionuclides from the U series, Th series and ^{40}K are the most important contributors to the gamma absorbed dose rate. Then:

$$\frac{dD}{dt} = \frac{dD}{dt}(\text{U series}) + \frac{dD}{dt}(\text{Th series}) + \frac{dD}{dt}(^{40}\text{K}) \quad (1)$$

The values of the gamma absorbed dose rate, dD/dt in $Gy.y^{-1}$, for every gamma emitter, will be determined knowing its concentration $C(Bq.cm^{-3})$ in the piles by the expression:

$$\frac{dD}{dt} = C \times DRF \quad (2)$$

DRF being the dose rate factors, in $(Gy.y^{-1})(Bq.cm^{-3})^{-1}$, whose values depend on the energies of the gamma emissions, the geometry and the distribution of radionuclides in the source.

Kocher and Sjoreen[13] have published the values of dose rate conversion factors for monoenergetic sources between 0.01 MeV and 3 MeV, under the same hypotheses of extension and uniformity in the source as in this work. The validity of this model for calculating the dose rate has been verified by several workers whose predictions are very similar to the dose rates obtained from experimental measurements[14]. Then, using these values, and considering in every series the existence of secular equilibrium between the daughters of short half-life and their progenitors, but not the existence of total secular equilibrium between all the radionuclides of each natural series, as it can easily be observed from the experimental values shown in the previous section, we can obtain:

$$\frac{dD}{dt}(^{238}\text{U series}) = 1.71 \times 10^{-5}\, C(^{238}\text{U}) + 1.05 \times 10^{-7}\, C(^{230}\text{Th}) + 2.97 \times 10^{-3}\, C(^{226}\text{Ra}) + 4.62 \times 10^{-7}\, C(^{210}\text{Pb}) \quad (3)$$

$$\frac{dD}{dt}(^{232}\text{Th series}) = 3.87 \times 10^{-8}\, C(^{232}\text{Th}) + 1.51 \times 10^{-3}\, C(^{228}\text{Ra}) + 2.30 \times 10^{-3}\, C(^{228}\text{Th}) \quad (4)$$

$$\frac{dD}{dt}(^{40}\text{K}) = 2.69 \times 10^{-4}\, C(^{40}\text{K}) \quad (5)$$

But from the general concentrations determined in phosphogypsum, it is known that the concentrations of ^{234}U, ^{210}Pb and ^{230}Th are either lower or, in extreme cases, slightly higher than the concentrations of ^{226}Ra. In the same way, it can be expected that both activity concentrations of ^{232}Th and ^{228}Th in the phosphogypsum are going to be very similar. These factors allow us to simplify the Equations 3, 4 and 5 to:

$$\frac{dD}{dt}(\text{U series}) = 1.71 \times 10^{-5}\, C(^{238}\text{U}) + 2.97 \times 10^{-3}\, C(^{226}\text{Ra}) \quad (6)$$

$$\frac{dD}{dt}(\text{Th series}) = 1.51 \times 10^{-3}\, C(^{228}\text{Ra}) + 2.30 \times 10^{-3}\, C(^{228}\text{Th}) \quad (7)$$

$$\frac{dD}{dt}(^{40}\text{K}) = 2.69 \times 10^{-4}\, C(^{40}\text{K}) \quad (8)$$

being the DRF expressed in $(Gy.y^{-1})(Bq.cm^{-3})^{-1}$.

Table 1. Activity concentrations ($Bq.kg^{-1}$) of the different radionuclides determined in the superficial (S) and deeper (D) phosphogypsum samples.

Sample	^{238}U	^{235}U	^{234}U	^{226}Ra	^{210}Po	^{228}Ra	^{40}K	^{228}Th
1S	111 ± 7	7.4 ± 0.5	104 ± 7	336 ± 18	392 ± 11	<12	<49	<8
1D	117 ± 10	11.7 ± 2.1	125 ± 11	506 ± 26	645 ± 13	<9	<43	<3
2S	107 ± 23	6.5 ± 2.5	115 ± 20	465 ± 24	345 ± 13	<4	<49	<3
2D	270 ± 14	13.5 ± 0.7	253 ± 14	957 ± 50	793 ± 70	<17	<67	<3
3S	290 ± 15	9.1 ± 1.6	296 ± 15	861 ± 45	550 ± 25	<12	<47	<3
3D	196 ± 17	8.5 ± 2.2	226 ± 20	483 ± 25	697 ± 34	<9	<44	<3
4S	161 ± 14	7.0 ± 1.8	161 ± 14	339 ± 20	451 ± 22	<12	<50	<3
4D	619 ± 25	20.7 ± 2.3	620 ± 26	1220 ± 63	794 ± 26	<27	<85	<4
5S	138 ± 14	6.2 ± 1.1	136 ± 14	430 ± 22	544 ± 64	<12	<51	<9
5D	133 ± 16	6.1 ± 1.2	121 ± 15	530 ± 28	428 ± 38	<4	<56	<3
6S	171 ± 15	8.1 ± 1.5	179 ± 15	471 ± 25	149 ± 14	<5	<66	<4
6D	185 ± 14	7.0 ± 1.5	196 ± 15	475 ± 25	681 ± 23	<9	<46	<3
7S	170 ± 14	6.0 ± 1.5	176 ± 14	481 ± 25	448 ± 21	<10	<46	<3
7D	154 ± 14	6.4 ± 1.6	150 ± 14	651 ± 34	1577 ± 170	<5	<67	<4

Then, if we assume an average density for the phosphogypsum sample of 1.25 g.cm^{-3} and as average and representative values of the needed concentrations in the phosphogypsum the values shown in Table 2, the gamma absorbed dose rate, dD/dt, for every series, and the total will be:

$$\frac{dD}{dt}\,(\text{U series}) = 2.18\ \text{mGy.y}^{-1} \quad (9)$$

$$\frac{dD}{dt}\,(\text{Th series}) = 3.23 \times 10^{-2}\ \text{mGy.y}^{-1} \quad (10)$$

$$\frac{dD}{dt}\,(^{40}\text{K}) = 1.86 \times 10^{-2}\ \text{mGy.y}^{-1} \quad (11)$$

$$\frac{dD}{dt}\,(\text{Total}) = 2.23\ \text{mGy.y}^{-1} \quad (12)$$

This last value is about six times higher than the average obtained from a worldwide typical soil.

The validity of the model used, and consequently the verification of the average calculated dose rate, has been performed by measurements *in situ* using the environmental dose rate meter. The values obtained at different places in the gyp-stacks are shown in Table 3, being the average dose rates in total concordance with those calculated from the model. Also, it is possible to observe a relatively high dispersion of the individual values, which might be expected due to the verified non-homogeneous distribution of the radionuclides in the phosphogypsum piles.

In Table 4 the contribution is shown to the gamma absorbed dose rate from the different radionuclides (and its short-life daughter in secular equilibrium) of the phosphogypsum piles deduced from the model calculation. Looking at this table it can be seen that the main problem associated with the phosphogypsum storage is its content of ^{226}Ra, and its decay to ^{222}Rn that can emanate from the piles into the atmosphere increasing its potential radiological hazard. Concerning this last point it is interesting to note that Hull and Burnett[3] in one of their studies done about Florida gyp-stacks have determined that the loss of ^{222}Rn from the phosphogypsum in the field is less than 10%, much less important than that deduced from laboratory measurements. These authors explain this fact indicating that the ^{222}Rn emanation from the gyp-stacks is probably impeded by surface crust, which results from compactation and recrystalisation of phosphogypsum. These surface crusts were observed in the extensive piles sited in Huelva when the sampling in this work was carried out.

Table 2. Average values of activity concentrations (Bq.kg^{-1}) of the radionuclides used in the estimation of the average gamma absorbed dose rate in air at 1 m above the ground.

^{238}U	^{226}Ra	^{40}K	^{228}Ra	^{228}Th	^{210}Pb
202	587	55	11	4	607

CONCLUSIONS

High concentrations of radionuclides belonging to the U series (specially ^{226}Ra and ^{210} Pb-^{210}Po) have been determined in samples collected in phosphogypsum piles, formed as a way of storage of the main by-product associated with the phosphoric acid production.

These gyp-stacks, which cover an area of 4.5×10^6 m^2 in the surroundings of some fertiliser factories in SW Spain, constitute a clear radiological anomaly. As a way to show the radiological importance of these phosphogypsum piles, the absorbed dose rate at 1 m above the

Table 4. Contribution to the gamma absorbed dose rate (mGy.y^{-1}) at 1 m above ground from the natural radionuclides in secular equilibrium with their daughters for the phosphogypsum piles.

Radionuclide	Contribution (mGy.y^{-1})	Percentage of total
^{238}U	0.00	0.0
^{226}Ra	2.18	97.8
^{228}Ra	0.02	0.9
^{228}Th	0.01	0.4
^{40}K	0.02	0.9
Total	2.23	100.0

Table 3. Gamma absorbed dose rates (mGy.y^{-1}) at 1 m height above ground measured using an environmental dose rate meter in the 15 selected zones from the gyp-stacks.

D1	D2	D3	D4	D5	D6	D7	D8
3.09	3.35	2.93	2.79	3.46	3.14	2.26	2.07
D9	D10	D11	D12	D13	D14	D15	
2.18	1.83	1.93	1.98	1.76	2.56	1.88	

Average dose = 2.48 ± 0.15 mGy.y^{-1}

zones due to its gamma emissions have been determined either experimentally (using an environmental dose rate meter) or by calculation from the radionuclide activity concentrations applying a simple model. The results obtained by both methods are in agreement, the gamma absorbed dose rates being six times higher than values obtained from a worldwide typical soil.

ACKNOWLEDGEMENTS

The authors are grateful to Mr Jesús González, Mr Juan Luis Aguado, Mr Enrique Gutiérrez and Mr Santiago de Paz from University of Huelva for their assistence in carrying out the alpha spectrometric determinations. Financial support by the Agencia de Medio Ambiente (Junta de Andalucía) is also specially acknowledged.

REFERENCES

1. Bolívar, J. P., García-Tenorio, R. and García-León, M. *Fluxes and Distribution of Natural Radionuclides in the Production and Use of Fertilizers*. App. Radiat. Isot. **46**, 717–718 (1995).
2. Bolívar, J. P., García-Tenorio, R. and García-León, M. *On the Fractionation of Natural Radioactivity in the Production of Phosphoric Acid by the Wet Acid Method*. J. Radioanal. Nucl. Chem. Lett. **214**, 77–88 (1996).
3. Hull, C. D. and Burnett, W. C. *Radiochemistry of Florida Phosphogypsum*. J. Environ. Radioact. **32**, 213–238 (1996).
4. Martínez-Aguirre, A. and García-León, M. *The Distribution of U, Th and ^{226}Ra Derived from the Phosphate Fertilizers Industries on an Estuarine System in Southwest Spain*. J. Environ. Radioact. **22**, 155–177 (1994).
5. Bolívar, J. P., García-Tenorio, R. and García-León, M. *Enhancement of Natural Radionuclides in Soils and Salt-marshes Surrounding a Non-nuclear Industrial Complex*. Sci. Total Environ. **173/174**, 125–136 (1995).
6. McDonald, P., Baxter, M. S. and Scott, E. M. *Technological Enhancement of Natural Radionuclides in the Marine Environment*. J. Environ. Radioact. **32**, 67–70 (1996).
7. Kouloheris, A. P. *Chemical Nature of Phosphogypsum as Produced by Various Wet Phosphoric Acid Process*. In: Proc. Int. Symp. on Phosphogypsum, Buena Vista Lake, Florida, USA. Eds D. P. Boris and P. W. Boody (Florida Institute of Phosphate Research), pp. 8–35 (1980).
8. Harada, K., Burnett, W. C., Cowart, J.P. and LaRock, P. A. *Polonium in Florida Groundwater and its Possible Relationship to the Sulphur Cycle and Bacteria*. Geochim. Cosmochim. Acta **53**, 143–150 (1989).
9. Hallstadius, L. *A Method for Electrodeposition of Actinides*. Nucl. Instrum. Methods **223**, 226–228 (1984).
10. El-Daoushy, F., Olsson, K. and García-Tenorio, R. *Accuracy Parameters in Alpha Spectrometry for Lead-210 Studies*. Hydrobiologia **214**, 43–52 (1991).
11. Bolívar, J. P., García-Tenorio, R. and García-León, M. *A Generalized Transmission Method for Gamma-efficiency Determinations in Soil Samples*. Nucl. Geophys. **8**, 485–492 (1994).
12. Tso, M. W. and Leung, J. K. C. *Radioecological Impact of Coal Ash from the Power Plants in Hong-Kong*. J. Environ. Radioact. **30**, 1–14 (1996).
13. Kocher, D. C. and Sjoreen, A. L. *Dose Rate Conversion Factors for External Exposure to Photon Emitters in Soil*. Health Phys. **43**, 193–205 (1985).
14. Baeza, A., Del Río, L. M., Jiménez, A., Miró, C. and Paniagua, J. M. *Natural and Man-Made Distribution in Soils of Cáceres. Dose Commitments due to External Radiation*. In: Low-Level Measurements of Radioactivity in the Environment: Technique and Applications. Proc. III Int. Summer School, Huelva (Spain). Eds M. García-León and R. García-Tenorio (World Scientific Company) pp. 285–297 (1994).