Valorization of an Inorganic Industrial Waste for Manufacturing Sulfur Polymer Cement

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INTRODUCTION

Phosphogypsum (PG), $CaSO_4{\cdot}2H_2O$, is a by-product coming from the processing of fluoroapatite, phosphate rock, resulting in H_3PO_4 production. Phosphate rocks contain high concentrations of some metals and natural radionuclides from ^{238}U decay-series, in secular equilibrium, which are about 50 times higher than the ones in typical soils. During the industrial process a fractionation of radioelements contained in phosphate rocks is produced. Only the 15 % of the worldwide PG production is recycled (Garg & Jain, 2010). The 85 % of remaining is deposited without any treatment in regulated stacks, and it may have a negative impact on the environment. On the other hand, sulfur polymer cement (SPC) is a civil engineering material, that have recently emerged as stabilizing agent for various waste (López et al., 2011). This paper is focused on the valorization of phosphogypsum in a sulfur polymer cement.

EXPERIMENTAL

SPC samples were obtained by a mix of different proportions of phosphogypsum, sulfur, gravel, sand and a thermoplastic material used as modified sulfur containing polymer (Table 1). The SPC samples were manufactured according to López et al. (2011). Each sample was called as SPC X-Y where "X" and "Y" are the percentage % wt of elemental sulfur and PG in the mixtures respectively. Morphology and microstructural characterization of samples were performed in a Hitachi S2100 scanning electron microscope (SEM).

The mechanical properties of the SPCs samples cured at ambient temperature for 1 day of age, were measured according to UNE 196-1:2005 standard.

The radioactive characterization was carried out by using a gamma spectrometry system with a XtRa coaxial germanium detector (Canberra). The detector was coupled to a conventional electronic chain, including a multichannel analyser and was shielded with Fe 15 cm thick. The method to measure the radon potential and the emanation factors is described by López-Coto et al. (2009).

The equation of radon conservation in the building material has allowed us to develop a 3D model of diffusive transport in porous media. This model has been solved for two geometries: a block of 0.04x0.04x0.16 m^3 and a plate of 1x1x0.04 m^3, using a numerical algorithm based on finite elements on an unstructured tetrahedral mesh.

Knowing the exhalation rate of the building materials used to construct a specific room, it is possible by modelling to estimate the expected radon concentration in this room under certain ventilation conditions. In this sense, it has been applied a simple model of radon accumulation in a standard room of 5x5x2 m^3 coated on all sides by plates of the same material.

RESULTS AND DISCUSSION

The morphology appearance of the surface crack of PG-SPC samples is shown in Fig. 1. The plasticized sulfur covers homogeneously the rounded grains of arid and laminar crystals of phosphogypsum, formatting a solid matrix with low porosity (Fig. 1).

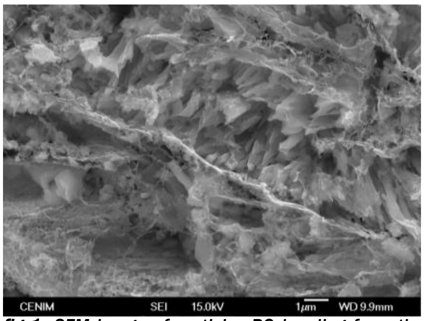

fig 1. SEM image of particles PG bonding from the plasticized sulfur in SPC 26-40 sample.

The compressive strength of the PG-SPC has a value between 49 and 62 MPa, and it is function of the PG content. The C_s values are similar to the SPC reference (58 MPa).

Table 2 shows the radionuclide concentration of PG and SPC samples. The radionuclides with the highest activity concentration in the SPC samples are ^{226}Ra (and its daughters of small half live: ^{222}Rn ^{218}Pb, ^{218}Bi, ^{214}Pb, ^{214}Bi, etc.) and ^{40}K. There is a good linear correlation between PG added and the activity concentration of ^{226}Ra (y=5.49 + 8.25 R^2=0,9988). To the PG value of x=0%, the activity concentration obtained is very low, around 8 $Bq{\cdot}kg^{-1}$ of ^{226}Ra, similar to ^{226}Ra activity concentration in SPC 21-0. If we consider x=100%, pure PG, it is obtained an activity concentration for ^{226}Ra of 557 $Bq{\cdot}kg^{-1}$, value very similar to indicated in Table 2 for PG sample, 589

Samples	Sulfur (S)	Gravel	Sand	PG	STX™	S/PG
SPC 21-0*	21.0	23.1	46.1	0.0	2.1	0.00
SPC 17-10	17.0	23.8	47.5	10.0	1.7	1.70
SPC 19-20	19.0	19.7	39.4	20.0	1.9	0.95
SPC 21-30	21.0	15.6	31.3	30.0	2.1	0.70
SPC 26-40	26.0	10.5	20.9	40.0	2.6	0.65
SPC 30-50	30.0	5.7	11.3	50.0	3.0	0.60

*Table 1. Composition of SPC samples (%wt.) and sulfur/PG ratios. Gravel/sand=0.5; Sulfur/STX™=10*Calcium carbonate (99.5% purity Panreac) in substitution of PG.*

palabras clave: Fosfoyeso, Radón, Microencapsulación, Cementos Poliméricos de Azufre

key words: Phosphogypsum, Radon, Microencapsulation, Sulfur Polymer Concrete

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Code	SPC 21-0	SPC 17-10	SPC 19-20	SPC 21-30	SPC 26-40	SPC 30-50	PG
% PG	0	10	20	30	40	50	100
^{210}Pb	8.0 ±0.6	70 ±5.0	143 ±9.0	219 ±13.0	264 ±16.0	340 ±20.0	624 ±37.0
^{238}U (^{234}Th)	12 ±2.0	21 ±2.0	12 ±2.0	38 ±3.0	50 ±4.0	60 ±4.0	97 ±6.0
^{232}Th (^{212}Pb)	9.1 ±0.6	9.4 ±0.7	8.6 ±0.6	8.1 ±0.5	5.9 ±0.4	5.8 ±0.4	8.2 ±1.0
^{226}Ra	7.4 ±0.5	63 ±4.0	115 ±7.0	179 ±11.0	226 ±13.0	282 ±17	589 ±34.0
^{228}Th	8.8 ±0.8	8.7 ±0.7	<6	6.8 ±0.7	7.3 ±0.6	6.1 ±0.6	7.8 ±0.7
^{228}Ra (^{228}Ac)	8.2 ±0.8	8.6 ±0.8	8.8 ±0.8	6.9 ±0.7	< 4	<4	8 ±1.0
^{40}K	580 ±30.0	528 ±32.0	394 ±24.0	347 ±21	239 ±15.0	143 ±10.0	<18
Index	0.26	0.43	0.56	0.75	0.85	1.01	2.01

Table 2. *Radionuclide concentration of SPC –PG samples and PG (Bq·kg^{-1}).*

Bq·kg^{-1}.
The activity concentration index (I) was calculated (Ec. 1):

$$I=[^{226}Ra]/300+[^{228}Ra]/200+[^{40}K]/3000 \quad (1)$$

Where [^{226}Ra], [^{228}Ra], [^{40}K] are, respectively, the activity concentrations in the building material considered, expressed in Bq·Kg^{-1}**.** The activity concentration index (I) in the studied samples agrees with the EU references values, in the range 0.3 – 1 mSv·a^{-1} (Table 2) (EC, 1999). Only SPC 30-50, with the 50% of PG, presents an I value around 1, so this could not be used in bulk amounts.

It has been carried out by modelling a simulation of a block of polymer cement (SPC 30-50) that emanates through all its sides excepting for the base (0.04x0.16 m^2). The blocks do not have an uniform radon exhalation rate, showing the geometry effect of this parameter (Fig. 2). In turn, the mean value for radon exhalation throughout its surface in contact with air is 3.6 ± 1.6 Bq·m^{-2}·h^{-1}, very similar to the experimental values ones.

	E	*σ*	*C$_{Rn}$ (λ$_v$ = 2 h^{-1})*	*C$_{Rn}$ (λ$_v$ = 0.1 h^{-1})*
SPC 17-10	*4.0*	*0.5*	*4*	*67*
SPC 19-20	*4.4*	*0.5*	*4*	*74*
SPC 21-30	*8.7*	*1.1*	*8*	*146*
SPC 26-40	*7.5*	*0.9*	*7*	*125*
SPC 30-50	*11.7*	*1.4*	*10*	*196*

Table 3. *Radon exhalation rate, E (Bq m^{-2} h^{-1}), of a plate (1x1x0.04 m^3) and the expected radon concentration, C$_R$ (Bq·m^{-3}), in a standard room.*

This model was applied to different plates 1x1x0.04 m^3 made off SPC-PG samples, the exhalation rates range from 2 to 12 Bq·m^{-2}·h^{-1} (Table 4), being of the same order of magnitude or slightly higher of typical building materials (1–10 Bq·m^{-2}·h^{-1}).

The plate made with SPC 30-50 presents the highest mean values for the exhalation rate, 11.7 ± 1.4 Bq·m^{-2}·h^{-1}, assuming an exhalation only in one side; it is due to the highest Rn Pot values, 30.6 Bq·kg^{-1}. Fig. 3 shows the radon exhalation rates obtained for different surface points of plate SPC 30-50; the highest values are found near the edges of the plate. Thus, the central part of the plate presents a value of 9 Bq·m^{-2}·h^{-1}, while their edges have values until above 15 Bq·m^{-2}·h^{-1}.

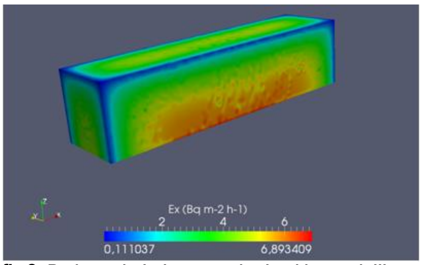

fig 2. *Radon exhalation rate obtained by modelling a specimen of 0.004 x 0.004 x 0.16 m^3 made with SPC 30-50 sample.*

The expected radon concentration inside a standard room (5x4x2.5 m^3) built with the plates (Fig. 3) is presented in Table 3. In the standard room with a good ventilation (air enhance, λ$_v$ = 2 h^{-1}), the highest expected radon concentration is reached inside the room with SPC 30-50, C$_{Rn}$=10 Bq·m^{-3}, but this value did not exceed the average radon concentrations to 200 Bq·m^{-3}, reference value in the EU for new houses. Under poor ventilation (λ$_v$ = 0.1 h^{-1}) the average radon concentrations increase. In SPC 30-50 the radon concentration achieved was 196 Bq·m^{-3}, very similar to the reference value in the EU, 200 Bq·m^{-3}.

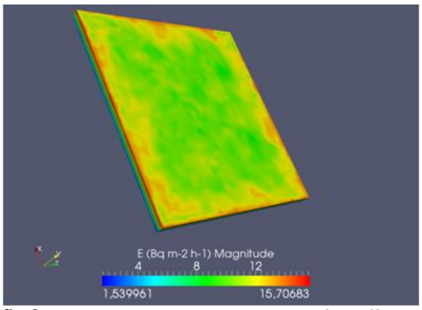

fig 3. *Radon exhalation rate obtained for different surface points of plate (1 x 1 x 0.04 m^3) of SPC 30-50 samples.*

CONCLUSIONS

SPC permitted the stabilization and solidification of PG with a low radionuclide. The incorporation of PG to the SPC does no significantly change the physical and mechanical properties of SPC when the PG is added in the 10-40% weight range. Activity concentration indices in the SPC-PG samples are lower than reference values. Therefore, these SPC-PGs can be used without radiological restrictions in manufacture building materials.

ACKNOWLEDGEMENTS

To the Spanish National R&D&I Plan (Project CTQ200802012/PPQ). Dr. I. García-Díaz to the MECC for the contract (Ref. FPDI-2013-16391) co-financed by the European Social Fund.

REFERENCES

Garg, M. & Jain, N., (2010) Waste gypsum from intermediate dye industries for production of building materials, Constr. Build. Mater., **24**, 1632-1637.

Lopez, F.A., Gázquez, M., Alguacil, F.J., Bolívar, J.P., García-Díaz, I., Lopez-Coto, I. (2011) Microencapsulation of phosphogypsum into a sulfur polymer matrix: Physico-chemical and radiological characterization. J. Hazard. Mat., **192**, 234-245.

López-Coto, I., Mas, J.L., Bolivar, J.P., García-Tenorio, R. (2009) A short time method to measure the radón potential of a porous material. Appl, Radiat. Isotopes, **67**, 133-138.

EC, Office European Commission Report on Radiological Protection Principles concerning the natural radioactive of building materials, Radiation Protection 112, Official Publications of the European Communities, Luxembourg, 1999.