



Microencapsulation of phosphogypsum into a sulfur polymer matrix: Physico-chemical and radiological characterization

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ABSTRACT

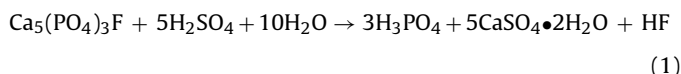
The aim of this work is to prepare a new type of phosphogypsum-sulfur polymer cements (PG-SPC) to be utilised in the manufacture of building materials. Physico-chemical and radiological characterization was performed in phosphogypsum and phosphogypsum-sulfur polymer concretes and modeling of exhalation rates has been also carried out. An optimized mixture of the materials was obtained, the solidified material with optimal mixture (sulfur/phosphogypsum = 1:0.9, phosphogypsum dosage = 10–40 wt.%) results in highest strength (54–62 MPa) and low total porosity (2.8–6.8%). The activity concentration index (*I*) in the PG-SPC is lower than the reference value in the most international regulations and; therefore, these cements can be used without radiological restrictions in the manufacture of building materials. Under normal conditions of ventilation, the contribution to the expected radon indoor concentration in a standard room is below the international recommendations, so the building materials studied in this work can be applied to houses built up under normal ventilation conditions.

Additionally, and taking into account that the PG is enriched in several natural radionuclides as ²²⁶Ra, the leaching experiments have demonstrated that environmental impact of the using of SPCs cements with PG is negligible.

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1. Introduction

Phosphogypsum (PG), CaSO₄·2H₂O, is a by-product coming from the processing of fluoroapatite resulting in H₃PO₄ production. In the process, fluoroapatite is dissolved using sulfuric acid. Phosphoric acid (PA), phosphogypsum, and hydrofluoric acid are obtained:



Phosphate rocks contain high concentrations of some metals as As, Cd or Sr, and natural radionuclides from ²³⁸U decay-series, in secular equilibrium, which are about 50 times higher than the

ones in typical soils [1,2]. During the industrial process is produced a fractionation of radioelements contained in PR. In the factory of Huelva (Southwestern Spain), ²²⁶Ra remains in PG (practically 100%), ²¹⁰Pb–²¹⁰Po (about 90%), and ²³⁰Th (70%) [3].

World PG production is around 200–280 × 10⁶ t per year [4,5]. Spanish fertilizer industry produces annually about 3 × 10⁶ t of PG, which is the result of processing 2 × 10⁶ t of phosphate rocks [6]. PG is deposited in regulated stacks, which may have a negative impact on the environment, being necessary a valorization and recycle of phosphogypsum.

Nowadays a number of researches are focused on the search of new uses of PG: (1) agricultural fertilizer or for soil stabilization amendments [7–10]; (2) cement industry as a setting regulator in place of natural gypsum [11–13], in the gypsum industry to make gypsum plaster [14,15], as mineralizer in the burning Portland cement clinker (PCC) [16], as raw material in the raw mix of cement [17–19] and in other binder materials [20–23]. Only the 15% of the world-wide production is recycled [1,4,6].

In this sense, we have studied a new application of PG in civil engineering, consisting in to use this by-product as additive of sulfur polymer cement (SPC). The SPC and SC (sulfur cement) has studied during last three decades [24–26], because of its high strength and excellent corrosion resistance.

Abbreviations: PR, phosphate rock; PG, phosphogypsum; PCC, portland cement clinker; SPC, sulfur polymer concrete; PG-SPC, phosphogypsum-sulfur polymer concrete; STXTM, sulfur modified; *I*, external risk index; Ra(eq), equivalent radium concentration; *A_c* (%), coefficient of absorption with respect to the pH; *L_c* (%), leaching coefficient for ²³⁸U and ²¹⁰Po at the different pHs.

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At different temperature sulfur presents two forms, orthorhombic (S_{α}), which is stable form of sulfur between 96 °C and ambient temperature and monoclinic (S_{β}) which is the form stable between 96 °C and the melting point of sulfur. Upon cooling to room temperature, the S_{β} quickly begins to revert to the α form, which is the form stable under ordinary conditions of temperature and pressure. Since the S_{α} form is denser than S_{β} and high stress is induced in the material by solid sulfur shrinkage, disappearing the plastic properties of sulfur. Due to this fact, the durability of this type of material was very poor and most materials failed in less than one month, especially in moist environments and when subjected to thermal cycling.

In this sense, the development of modern chemically resistant SPC and SC has taken place during the last three decades. The key to this development came with the discovery of a new technique to stabilize sulfur by preventing the indicated allotropic transformation which led to premature failure, which allowed to a new class of chemically resistant materials formulated of the base of several additives.

The most common plasticizing studied is dicyclopentadiene (DCPD) or a combination of DCPD and dipentene [27–29]. Also a polyolefinic material was used as plasticizing agent [25]. A plasticized concentrate or modified sulfur, called STXTM is first formulated from the polyolefin and elemental sulfur and then added to additional elemental sulfur and aggregates. This kind of elemental sulfur is denominated sulfur polymer concrete (SPC).

SPC has properties, which for certain applications are superior to OPC (Ordinary Portland Cement) [30], due to high durability and its fast setting time and rapid gain of high strength, achieving most of its mechanical strength in less than 1 day. Also SPC have recently emerged as stabilizing agent for various wastes [31–36].

Due to the relative high levels of natural radionuclides in the PG, an important radiation exposure could be received from building materials containing this by-product. The radiation exposure from the building material can be divided in both external (direct gamma radiation) and internal exposure (inhalation of ²²²Rn and its decay products). Different international recommendations propose reference values for the natural radionuclide concentrations in building materials. Publication No. 112 from monographic collection "Radiation Protection" issued by the European Union and defines the external risk index (I), also called activity concentration index, Eq. (2), to ensure that external gamma dose rate inside a room from building materials does not exceed 1 mSv per year.

$$I = C(^{226}\text{Ra})/300 + C(^{228}\text{Ra})/200 + C(^{40}\text{K})/3000, \quad (2)$$

where $C(^{226}\text{Ra})$, $C(^{228}\text{Ra})$ and $C(^{40}\text{K})$ are the activity concentrations for ²²⁶Ra, ²²⁸Ra and ⁴⁰K, respectively, in the building material considered, expressed in Bq kg⁻¹. This index should not exceed the value $I \leq 1$ for materials used in bulk amounts, e.g. concrete, or $I \leq 6$ for superficial and other materials with restricted use, e.g. tiles, boards, etc., to assure that the additional external dose received by occupants living in buildings constructed with these materials does not exceed the value limit of 1 mSv year⁻¹.

Other countries considered the equivalent radium concentration parameter, Ra(eq), which is shown in Eq. (3):

$$\text{Ra}(\text{eq}) = C(^{226}\text{Ra}) + 1.43C(^{228}\text{Ra}) + 0.077C(^{40}\text{K}), \quad (3)$$

where $C(^{226}\text{Ra})$, $C(^{228}\text{Ra})$ and $C(^{40}\text{K})$ are the activity concentrations for ²²⁶Ra, ²²⁸Ra and ⁴⁰K in Bq/kg, respectively. Conclusions obtained by both index are usually very similar.

The reference value for Ra(eq) in many countries for building materials is 370 Bq kg⁻¹ [37]. The radon-222 and its short-lived daughters contribution is on 50% of the total natural effective dose received by the population [38]. As a consequence, many countries have established reference levels for radon in houses and work places, being these values of 200 and 400 Bq m⁻¹, respectively.

Taking into account the previous considerations, we have stated two objectives. The first one has been to study the stabilization/solidification of PG, allowing its revalorization such as building materials in safe conditions with respect to their radioactivity levels. On the other hand, the second objective has been to characterize the mechanical properties of sulfur polymer cements manufactured with phosphogypsum, the study of the long-term stability and the evaluation of its radiological impact.

2. Experimental

2.1. Materials

The raw materials used for this study were a granular elemental sulfur (99.4 wt.%, size <60 μm, type Rubber Sul 10) supplied by Repsol IPF (Madrid, Spain), gravel (<6.3 mm) and a siliceous sand (<4 mm) were used as commercial mineral aggregated materials.

A modified sulfur containing polymer (STXTM supplied by StarcreteTM Technologies Inc. Québec, Canada) was used as thermoplastic material [33]. STXTM polymer improves fine sulfur crystal formation and grain size control, which supplies higher mechanical properties.

Phosphogypsum samples were supplied by the Fertiberia factory of Huelva in 2009. This PG samples were then dried at 50 °C for 48 h.

2.2. Sample preparation

The mixture of typical SPC's was listed in Table 1. The ratio of gravel/sand was maintained constant at 0.5. The ratio of sulfur/modified sulfur (STXTM) was maintained constant at 10 for all the samples. Prior research [35] has indicated that these relations are the better conditions for the viscosity and workability of the mixture. Similar results have been reported by other authors [36]. It should be noted that the percentage of modified sulfur plays an important role in the workability and mechanical strength of SPC [24].

Two types of samples were prepared: samples containing PG (PG-SPC) and reference sample (SPC) without PG addition.

Phosphogypsum SPC cements (PG-SPC) were prepared as follows. The aggregates (gravel/sand and phosphogypsum) were heated in the oven to 130–135 °C for 4 h. The specific amount of sulfur, gravel, sand and phosphogypsum were heated in a preheated mixing bowl where the temperature was controlled at 135–140 °C for 10 min. The heated mixture was properly mixed until a homogeneous viscous mixture was obtained. Then the modified sulfur was added with continuous mixing. Finally the mixture is stirred at 140–145 °C for 4–5 min to ensure the total fusion of the thicker particles. Temperature control is very important because temperatures higher than 145 °C may lead to side reactions between STXTM and sulfur, thus causing formation of high viscosity products and, hence, poor workability. A steel mold with dimension 40 mm × 40 mm × 160 mm was used. The molds were preheated to approximately 120 °C before adding the sulfur polymer cement, the material was compacted using a vibration of 3000 rpm for 30 s on a vibrating table. The storage of the molds was done at a room temperature. The specimens were de-molded at an age of 24 h after placement in steel molds.

Phosphogypsum has been added to the mixtures at dosages between 10 and 50 wt.%. A total of 5 PG-SPC were prepared, each of the samples were denominated as SPC X-Y where "X" is the percentage wt.% of elemental sulfur and "Y" is the percentage wt.% of phosphogypsum of the mixtures.

The SPC sample reference (called SPC-21) was manufactured similarly to the PG-SPC samples, but in this case, calcium carbonate

Table 1
The mix proportion of different SPC's (expressed as wt.%).

Samples	Elementalsulfur	Gravel	Sand	Phosphogypsum	Modified sulfur STX	Ratio sulfur/PG
SPC-21 (reference)	21.00	23.10	46.14	0	2.10	0.70
SPC-17-10	17.00	23.77	47.53	10.00	1.70	1.70
SPC-19-20	19.00	19.70	39.40	20.00	1.90	0.95
SPC-21-30	21.00	15.63	31.27	30.00	2.10	0.70
SPC-26-40	26.00	10.47	20.93	40.00	2.60	0.65
SPC-30-50	30.00	5.67	11.33	50.00	3.00	0.60

(99.5% purity, Panreac) was added as filler (10% of the mixture) in substitution of PG.

2.3. Sample characterization

The size distribution particle measurement of the PG was carried out by means on a Malvern Mastersizer 2000 laser diffractometer.

X-ray fluorescence (XRF) was employed to determine major elements, impurities and trace elements in PG and PG-SPC samples. The analysis was carried out in a Philips PW 1404.

Physical and mineralogical characterizations were performed on PG and PG-SPC samples by X-ray diffraction (XRD) and scanning microscopy (SEM).

Analyses of XRD were used to determine crystalline phases in PG, sulfur (S), modified sulfur (STXTM) and PG-SPC. In this work, a Bruker D8 Discover diffractometer with K α Cu radiation (30 mA current and 40 kV) was used. The patterns of diffraction were obtained in a 2 Θ scanning range from 10° to 100°, with 0.03° and 3 s of scan step and time, respectively.

Morphology and microstructural characterization of samples were performed using a Hitachi S2100 scanning electron microscope (SEM).

The mechanical properties of the SPCs cements, such as compressive strength (C_s) were measured according to the standard UNE 196-1:2005. The results were obtained as an average value of six measurements performed using a universal press Ibertest mod. Autotest 200-10-W. Compressive strength was measured for SPC and PG-SPC cured at ambient temperature for 1 day of age. It is not necessary for a longer period time, because it is clear that the 80% of its ultimate SPC's compressive strength was developed in 1 day [35,36].

The bulk (apparent) density of samples, ρ_b , was measured by a dry flow pycnometer (GeoPyc 1360). The skeleton (relative), ρ_s , and real (absolute), ρ_r , densities were measured by He displacement Pycnometer (AccuPyc 1330). Density values were used to determine total porosity (P_T), closed porosity (P_C) and open porosity to He, according to Eqs. (4)–(6):

$$P_T(\%) = \left[\left(1 - \frac{\rho_b}{\rho_r} \right) \right] \times 100, \quad (4)$$

$$P_C(\%) = \left[\left(1 - \frac{\rho_d}{\rho_r} \right) \right] \times 100, \quad (5)$$

$$P_{He}(\%) = [P_T - P_C]. \quad (6)$$

The total pore volume was determined by Eq. (7):

$$V_p = \left(\frac{1}{\rho_b} - \frac{1}{\rho_r} \right). \quad (7)$$

The coefficient of water absorption by capillarity (WAC) is a measure of water permeability. The WAC of the test materials was determined gravimetrically. Prismatic cement specimens with and without PG (SPC-21-30 and SPC-21, respectively) measuring 40 mm \times 40 mm \times 160 mm were dried at 50 °C in an oven until a constant mass was reached. They were then placed on a support grating in a dish supplied with a water leveller at room temperature. The water level was sufficient to wet only the lower surface of the test

specimens. The lower parts of the sides of the specimens adjoining the inflow face were sealed with an adhesive to prevent any water being absorbed into their surface pores. Mass data for each specimen were recorded over time until a constant mass was reached. All experiments were performed in triplicate.

2.4. Measurement of radionuclides

The radioactive characterization was carried out by using a gamma spectrometry system with an XtRa coaxial germanium detector (Canberra), which has a 38% relative efficiency, and FWHM of 0.95 keV at the 122 keV line of ⁵⁷Co and 1.9 keV at the 1333 keV line of ⁶⁰Co. The detector was coupled to a conventional electronic chain, including a multichannel analyzer and was shielded with Fe 15 cm thick. The samples were dried at 60 °C and grounded. The whole procedure of calibration and this gamma spectrometry system are described elsewhere [37].

2.5. Radon potential and bulk exhalation measurements

The radon exhalation of a material surface is the radon flow released through the available surfaces ($Bq\ m^{-2}\ s^{-1}$), which is influenced by the material geometry and the boundary conditions. On the other hand, the radon potential is defined as the radon concentration generated inside the material and that is available to be transported through its pores.

The method to measure the radon potential and the emanation factors is described by López-Coto et al. [38]. From growth curves of radon inside a closed chamber it is possible to calculate the exhalation rate of the block and, under specific experimental conditions, the radon potential of the tested material. From the radon in growth curve for each block in the accumulation chamber the exhalation rate of each specimen is determined. In addition, once crushed a portion of the specimen (about one-third), from a second measurement in the chamber for obtaining radon potential and the real emanation factor of the material used in each of the samples.

2.6. Radon transport simulations

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 40 mm \times 40 mm \times 160 mm and a plate of 1 m \times 1 m \times 0.04 m, which was carried out by 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 modeling to estimate the expected radon concentration in this room under certain ventilation conditions. In this sense, a simple model of radon accumulation has been applied in a standard room of 5 m \times 5 m \times 2 m coated on all sides by plates of the same material [39].

2.7. Accelerated leach test

The leaching of radionuclides from both SPC-21 and SPC-21-30 was tested in buffers of different pH. The test sample ($n = 15$)

Table 2
Chemical composition of raw materials (expressed as wt.%).

Component	Phosphogypsum	Gravel	Sand
SO ₃	52.41	0.27	–
CaO	40.30	57.83	0.42
F ⁻	3.34	1.54	–
SiO ₂	2.40	29.12	79.89
P ₂ O ₅	0.95	–	–
Al ₂ O ₃	0.40	1.27	10.75
Fe ₂ O ₃	0.23	0.80	0.74
Na ₂ O	0.13	–	1.78
TiO ₂	0.04	0.13	0.11
K ₂ O	0.03	0.25	5.30
MgO	0.04	0.63	0.26
CuO	0.01	–	–
SrO	0.09	0.05	–
ZrO ₂	0.01	0.02	–
BaO	0.02	0.02	0.05
LOI	2.40	7.86	8.90

dimensions were 40 mm × 40 mm × 160 mm. All samples were submerged in demineralized water for 24 h. They were then dried, weighed, and then again submerged for 21 days in 250 ml of buffer solutions at different pH (2–10) (Panreac) ($n = 3$ for each pH). After this time the samples were air-dried and weighed to make sure their weight had not changed by more than ±2 g compared to their starting weights. The samples were then again submerged in their respective buffers for another 21 days. At the end of this period they were again weighed and dried. The variation in weight ($P_{3i} - P_{1i}$) and the coefficient of absorption with respect to the pH (A_c) determined as follows:

$$A_c(\%) = \frac{P_{3i} - P_{1i}}{P_{1i}} \times 100, \quad (8)$$

where P_{3i} is the weight after 42 days of immersion, and P_{1i} the initial weight of each sample after immersion in water for 24 h.

After the 42-day experimental period the solutions were filtered and their radionuclide concentrations determined. ²¹⁰Po was determined by alpha spectrometry, and ²³⁸U by laser phosphorimetry. ²²⁶Ra, ²³⁴Th, ²³²Th, ⁴⁰K and ²¹⁰Pb were determined by gamma spectroscopy. The radionuclide concentrations of the buffers used in the initial concrete samples (before the leach tests) were also determined, and found to be close to the detection limits of the methods employed.

The radionuclide concentrations of the leachates were used to determine the leaching coefficient (L_c) for ²³⁸U and ²¹⁰Po at the different pHs according to Eq. (9) (see Table 11 for results):

$$L_c(\%) = \frac{A_L(\text{Bq l}^{-1})}{A_s(\text{Bq g}^{-1})} \times \frac{V_t(\text{l})}{P_{1i}(\text{g})} \times 100, \quad (9)$$

where A_L is the concentration of the corresponding radionuclide in the leachate (expressed in Bq l^{-1}), V_t is the total volume of the solution after 42 days (0.250 l in all cases), A_s is the concentration of the corresponding radionuclide in the concrete (expressed as Bq g^{-1}), and P_{1i} the weight of the concrete sample after 42 days of immersion in the corresponding buffer (expressed in g).

3. Results and discussion

3.1. Characterization of raw materials

The average chemical compositions for raw materials are shown in Table 2. Main contents of phosphogypsum are Ca and S (expressed as SO₃), as we expected (CaO and SO₃ is close to 90% of total). The major impurities in PG were SiO₂, P₂O₅, Fe₂O₃, Al₂O₃ and Na₂O, and, to a lesser extent, K₂O and TiO₂. It is important to note that P₂O₅ was also found in PG (0.96 wt.%), which remains in PG later the washing in the industrial process [40].

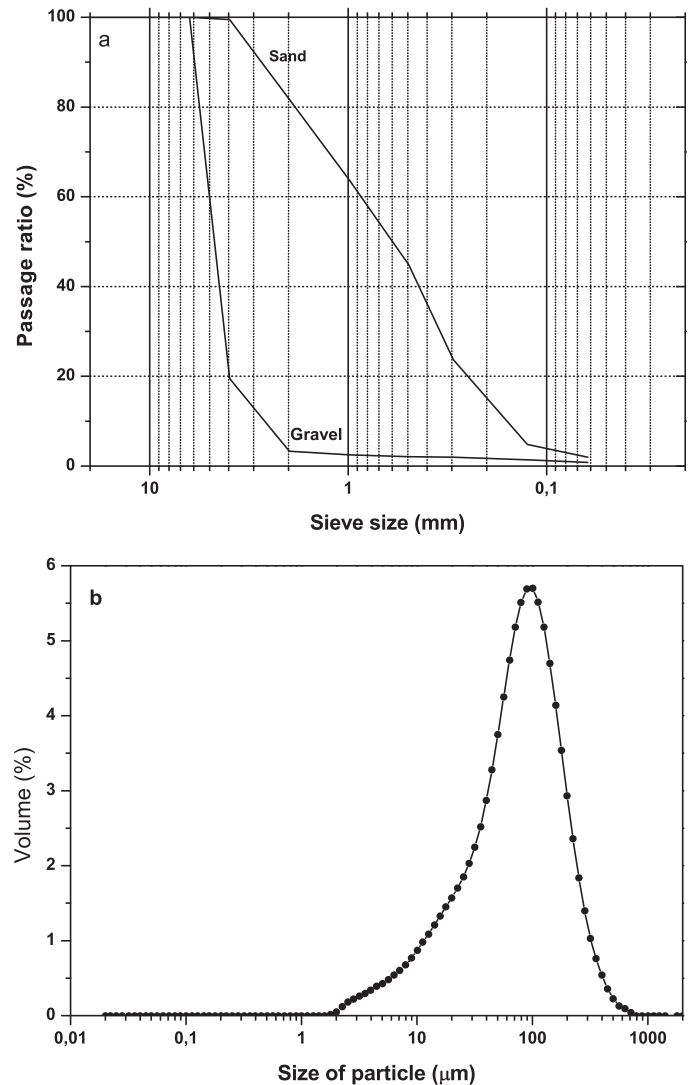


Fig. 1. The particle size distribution of raw materials. (a) Aggregates and (b) phosphogypsum.

Fig. 1a shows the percentage of particles, by mass %, in the gravel and sand, according to Spanish Standard for structural concretes [41]. Fig. 1b shows the percentage of particles of PG, by volume, between 1 and 1000 μm. The d_{50} value of the particle measured was equal or less than to the 53 μm.

Two crystalline phases can be clearly observed (Fig. 2); gypsum (JCPDS 00-033-0311), and bassanite (JCPDS 00-041-0224). The diffractogram shows a less intensity diffraction lines appearing at 26.64 (2θ) corresponding to the quartz (SiO₂) (JCPDS 00-046-1045).

Fig. 3 shows the XRD patterns for elemental sulfur and modified sulfur. In the elemental sulfur, the orthorhombic phase S_α (JCPDS 00-008-0247) is clearly observed. The modified sulfur exhibits a diffractogram similar to sulfur but with a lower crystallinity. Besides, the diffractogram shows diffraction lines at 22.8 and 27.8° (2θ), corresponding to phase S_β (JCPDS 00-034-0941). These lines can be better observed in the magnification set at the upper right corner of the figure.

The morphology of PG particles is shown in Fig. 4. The PG crystals exhibited shapes in the acicular form (a) and tables (b) and a well-defining crystalline structure with and rhombic shaped crystal.

Fig. 5 shows the morphological aspect of the modified sulfur (STXTM). Fig. 5a shows the myriad complex of interconnected ordered angular crystalline structures depicting almost perfect 45

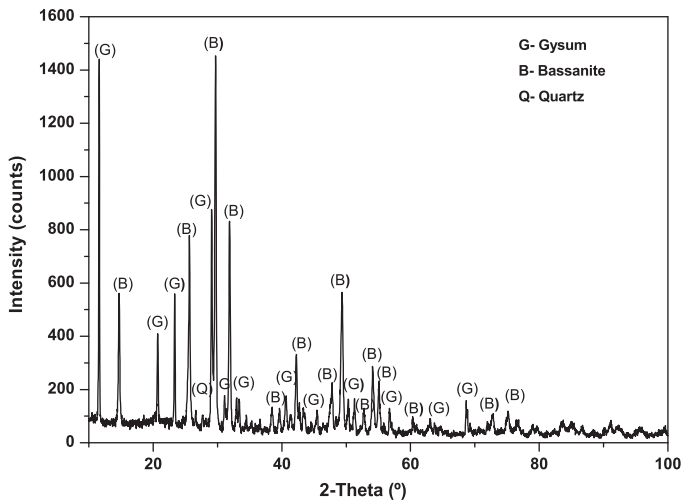


Fig. 2. XRD patterns of the phosphogypsum.

and 90° angles. The angular crystalline structures were conducive to structurally strong material. We can now observe under higher magnification that the structural strength is further complemented by additional bonds provided by the ciliated projections extending from each crystal into the matrix (Fig. 5b).

The morphological appearance of the mixture of elemental sulfur and modified sulfur after heating at 145°C and then cooling at room temperature is shown in Fig. 6. Fig. 6a corresponds to a compact and continuous structure of a polymeric plastic material. Similar ciliated filaments as those shown in Fig. 5b are visible. Different magnifications of ciliated filaments can be easily observed in Fig. 6b. The ciliated filaments are composed by micro particles of elemental sulfur (bar 150 nm) in a compact structure (Fig. 6c).

3.2. Characterization of phosphogypsum SPC cements

The macroscopic aspect of final product obtained by the PG-SPC can be seen in Fig. 7. The colour of the PG-SPC is similar to the one of initial PG, being observed macropores in all the sample surfaces. The presence of these macropores is due to the exit of occluded air within the SPCs. The air exit is carried out in the vibration compacting process. Probably, a longer vibration time yielded best results. The number of superficial macropores decreased as the PG content

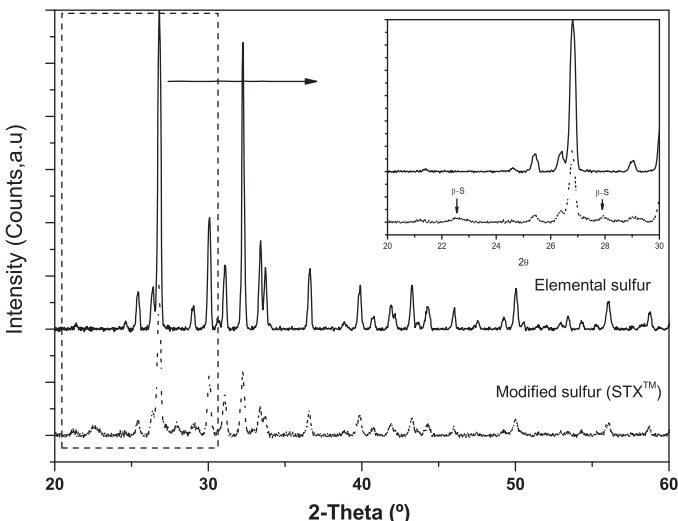


Fig. 3. XRD patterns of the elemental sulfur and modified sulfur (STX™).

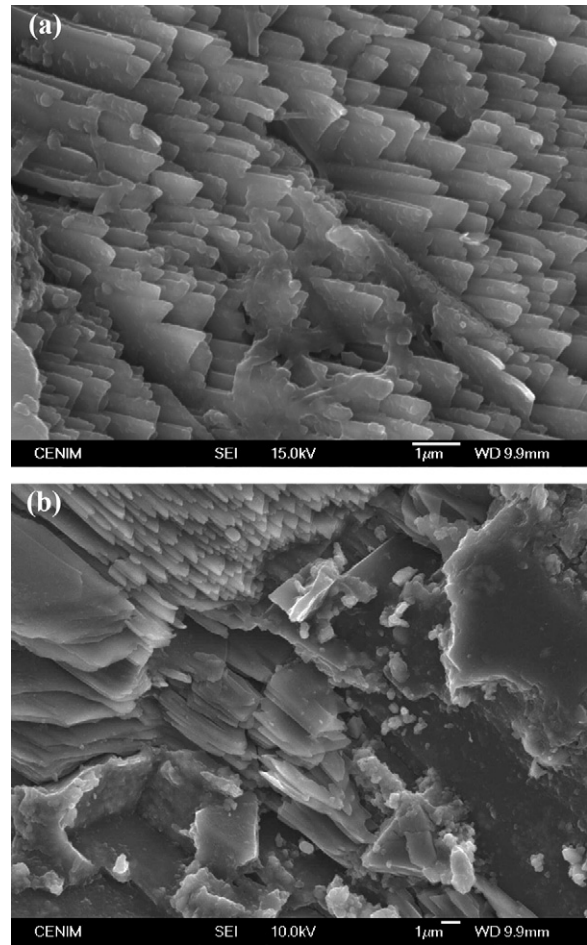


Fig. 4. Morphology of particles found in phosphogypsum: (a) acicular shape and (b) shape like tables.

in the SPC is increased. The presence of these macropores has a negligible effect on the physical properties of these materials.

Table 3 shows the results of the chemical analysis of the SPC samples. According to these findings the percentage of CaO , P_2O_5 and SO_3 increases with the content of phosphogypsum. However, the content of the SiO_2 , Al_2O_3 and Fe_2O_3 , fundamental constituents of the sand and gravel, is reduced as the percentage of phosphogypsum is increased.

Fig. 8 shows the XRD patterns of SPC-reference and PG-SPC. In the SPC-reference the crystalline phases are S_β (JCPDS 00-034-0941), quartz (SiO_2) (JCPDS 00-046-1045) and calcite (CaCO_3) (JCPDS 00-005-0586). The diffractogram shows a less intensity diffraction line corresponding to the cristobalite (SiO_2) (JCPDS 00-039-1425) and mogonite (SiO_2) (JCPDS 00-052-1425). The presence of calcite, cristobalite and mogonite can be attributed to the presence of gravel and sand in the SPC composition.

The crystalline phases presented in the PG-SPC finding indicated a similar mineralogy composition of the four samples. The diffraction lines are attributed to the quartz (SiO_2) (JCPDS 00-046-1045), anhydrite (JCPDS 00-037-1496), bassanite (JCPDS 00-041-0224), calcite (JCPDS 00-005-0586) and S_β (JCPDS 00-034-0941).

The morphology appearance of the fracture surface of PG-SPC samples can be seen in Fig. 9. Fig. 9a shows the bonding from the plasticized sulfur to the PG. The bonding and bridging is more pronounced as depicted in Fig. 9b. The plasticized sulfur covers homogeneously the rounded grain of arid and crystal lamina of phosphogypsum, formation of a solid matrix with low porosity (Fig. 9c) [43].

Table 3
Chemical composition of the SPC's cements (expressed as wt.%).

Component	SPC-21 (reference)	SPC-17-10	SPC-19-20	SPC-21-30	SPC-26-40	SPC-30-50
Na ₂ O	0.34	0.29	0.31	0.21	0.17	0.09
MgO	0.18	0.15	0.16	0.09	0.06	0.03
Al ₂ O ₃	2.71	2.52	2.42	1.43	1.15	0.65
SiO ₂	29.15	29.90	26.04	15.52	12.74	6.64
P ₂ O ₅	0.06	0.23	0.34	0.48	0.55	0.57
SO ₃	41.23	41.86	41.58	52.07	53.48	58.75
K ₂ O	1.90	1.67	1.62	0.91	0.79	0.35
CaO	23.33	21.66	25.79	27.29	29.07	31.29
TiO ₂	0.02	0.08	0.08	0.06	0.06	0.04
Cr ₂ O ₃	0.03	0.03	0.03	0.02	0.02	0.01
MnO	0.01	0.01	0.02	0.01	<	<
Fe ₂ O ₃	0.89	0.52	0.59	0.55	0.44	0.32
F ⁻	0.13	1.08	1.08	1.47	1.57	1.35
CuO	0.01	0.01	0.01	0.01	0.02	0.02
Rb ₂ O	0.02	0.01	0.01	<	<	<
SrO	0.01	0.02	0.03	0.04	0.05	0.06
ZrO ₂	<	0.01	<	0.01	<	<
BaO	0.02	0.03	0.03	0.02	0.02	0.01

The variation of the compressive strength (C_s) vs. content of phosphogypsum in the SPCs cements is shown in Fig. 10. The compressive strength of the PG-SPC has a value between 49 and 62 MPa, and it is function of the content of phosphogypsum in the mixed samples. The C_s values are similar to the valor of reference-SPC.

The mechanical strength presents a maximum at 20% of PG and from here it decreases as the phosphogypsum content increases in

the SPC. In general, the best mechanical properties are observed for the SPCs with 10–40% of PG.

Fig. 11 shows the desired optimum amount of sulfur to phosphogypsum ratios according to the mechanical strength of the PG-SPC. The obtained strength tends to increase as the sulfur/phosphogypsum ratio increases up to 0.9, when all the particles are coated with a thin layer of sulfur, which acts as a good binder for aggregate particles and finally leads to increase strength. However with a large addition of sulfur, the compressive strength decreases, because a further increment of sulfur increases the thickness of sulfur layers around the aggregate particles and leads to increased brittleness of the composite materials formed.

Compressive strength of PG-SPCs is typical for stabilization/solidification materials. López et al. [35] reported compressive strength of 54 and 58 MPa for metacinnabar SPC, with a rate sulfur/HgS of 0.4 and 2.6. These types of SPC are similar to phosphogypsum SPCs obtained in this work, the metacinnabar (HgS) was substitute for the phosphogypsum. Mohamed et al. [42] obtained compressive strength of 54 MPa for SPC with fly ash, obtaining the maximum strength with a relation sulfur/fly ash of 0.9. Lin et al. [32] showed that the SPC obtained from lead-contaminated wastes have a compressive strength of 48.5 MPa. Sandrolini et al. [36] reported that the compressive strength of SPC with a recycle aggregate coming from a ceramic industry is between 65 and 73 MPa.

The rapid hardening and early strength gain changed over time, resulting in a very high strength material with an average compression of 48–62 MPa [43]. As a reference material, it is worth nothing that for mortars made from Portland cement the compressive strength properties were found to be 22 MPa [44], value less than obtained from phosphogypsum SPC.

These results indicate that the polymeric matrix can incorporate high content of phosphogypsum with a relation sulfur/phosphogypsum of 0.9 without a significant modification of the mechanical properties.

Table 4 shows the values of density, total pore volume and porosity of the PG-SPC cements. A diminish of the density values (ρ_r , ρ_s and ρ_b) is observed as the phosphogypsum content increases in PG-SPC. The V_p and the porosity (P_T , P_C and P_{He}) diminish when the phosphogypsum content increases in SPC. Except in the SPC-30-50 where these values are similar to SPC-17-10, could be attributed to a less workability of the mixture and a defect of the melt phase to cover all the surface of all the grain of the prime materials. The values of density and porosity of PG-SPC are similar to SPC-reference.

Similar values of porosity have been obtained for other authors. Sandrolini et al. [36] reported a high value of total porosity of

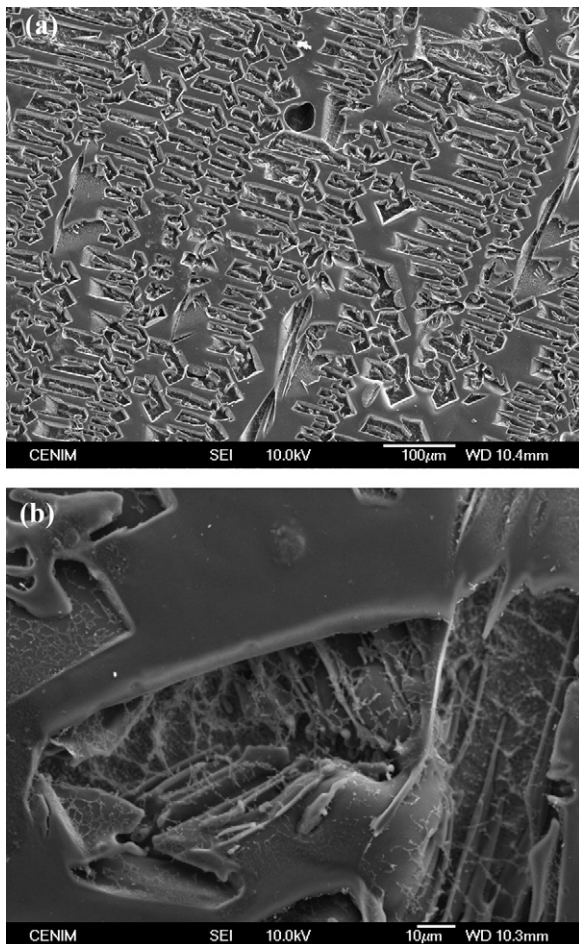


Fig. 5. SEM images of modified sulfur (STX®): (a) interconnected ordered angular crystalline structures and (b) magnification of the ciliated filaments.

Table 4Real (ρ_r), skeleton (ρ_s) and bulk (ρ_b) density, total pore volume (V_p) and total (P_T), close (P_C) and open (P_{He}) porosity.

Properties	SPC-21 (reference)	SPC-17-10	SPC-19-20	SPC-21-30	SPC-26-40	SPC-30-50
ρ_r (g cm ⁻³)	2.49	2.52	2.50	2.46	2.42	2.39
ρ_s (g cm ⁻³)	2.44	2.46	2.45	2.42	2.37	2.32
ρ_b (g cm ⁻³)	2.18	2.37	2.33	2.39	2.36	2.25
V_p ($\times 10^{-2}$) (cm ³ g ⁻¹)	1.65	2.51	2.92	1.19	1.05	2.60
P_T (%)	3.98	5.95	6.80	2.85	2.48	5.86
P_C (%)	2.39	2.38	2.00	1.63	2.07	2.93
P_{He} (%)	1.59	3.57	4.80	1.22	0.41	2.93

Table 5

Water absorption by capillarity as a function of time for cement with and without PG.

Sample	Water absorption (kg m ⁻²)			
	3 h	72 h	7 days	28 days
Reference (SPC-21)	0.07	0.20	0.30	0.90
SPC-21-30	0.10	0.16	0.20	1.20

10.2–10.7%, open porosity was of 6.0 and 7.0 and close porosity was of 1.8 and 4.0 by SPC where de graded of the SPC was substituted by a waste of the industry ceramic. López et al. [35] showed that the total porosity (2.88–1.97%), open porosity (1.44–1.40%) and close porosity (1.44–0.57%) of metacinnabar SPC obtained with 20 and 30% of mercury decreasing when the content on mercury increases.

These results showed that the incorporation of PG to the SPC does not significantly change the physical properties of SPC when the PG is added in the 10–40% weight range. However, a 50% addition of PG to the SPC decreased the compression strength and increased the porosity when compared with that of the reference material.

Table 5 shows the WAC results recorded. Being very small, they are in agreement with the porosity values for the cements (Table 4). After 28 days, the SPC-21-30 showed a WAC coefficient over 33% higher than that of the SPC-21. Both values, however, are smaller than those for concrete made from Portland cement. Khatib and Clay [45] report WAC coefficients of 5.0 kg m⁻² after 28 days of immersion in water for an ordinary Portland cement. Medeiros and Helene [46] reported WACs of 6.2 kg m⁻² at 28 days for a concrete made of Brazilian Portland cement (CPII E-02) (slag modified Portland cement). The use of a sulfur/modified sulfur mix, however, reduces the WAC coefficient, producing a very impermeable concrete.

3.3. Radiological characterization of samples

3.3.1. Activity concentration and index risk

Prior to possible use of these PG-SPC materials, preliminary radiological analyses have been carried out in order to reliably assess the radiation dose related to the use of these materials. Based on the findings it will be possible to decide whether these materials can be used for the given purposes from a radiological point of view.

Table 6

Radionuclide concentration of SPC, PG-SPC cements and phosfogypsum sample natural origin.

Code	SPC-21	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

From Table 6 it is evident that radionuclide with the highest activity concentration is ²²⁶Ra (and its daughters of small half-lives: ²²²Rn, ²¹⁸Pb, ²¹⁸Bi, ²¹⁴Pb, ²¹⁴Bi, etc.), and ⁴⁰K. Obviously, ⁴⁰K concentration decreases according to increases in the PG content of the sample, due to the very low content of potassium in PG (<18 Bq kg⁻¹ of ⁴⁰K, i.e., <0.06% of natural potassium).

The activity concentrations of ²³⁸U and ²²⁶Ra in the pure PG sample, around 100 and 600 Bq kg⁻¹, respectively, are in agreement with typical values given in the literature for PGs from Huelva [1,3,4], which are significantly higher than the average world-wide values from soils (25 Bq kg⁻¹ of ²³⁸U and daughters) [47]. At the same time the concentration of ⁴⁰K in all samples remains significantly below the world average of ⁴⁰K, 500 Bq kg⁻¹, only SPC-17-10 sample slightly exceeds this value.

Fig. 12 shows a strong lineal dependence ($r^2 = 0.9983$) between the percentage of PG added and the activity concentration of ²²⁶Ra. From this plot that can be obtained we also conclude that, SPC cement, without PG, present very low activity concentrations in natural radionuclides (obtained doing $x = 0\%$ PG), and giving around 8 Bq kg⁻¹ of ²³⁸U in secular equilibrium with its daughters. On the contrary, if we consider $x = 100\%$ (pure PG), an activity concentration for ²²⁶Ra of 560 Bq kg⁻¹ is obtained, value very similar to the one indicated in Table 6 for PG sample (589 Bq kg⁻¹). These considerations can be also used to ratify the radiometric measuring methods applied to the studied samples.

In relation to the radiological assessment, recommendations according to the radioactivity protection commission of EU are found in [48], which recommends a reference increment of effective dose in the range of 0.3–1 mSv a⁻¹.

Activity concentration index (I) in the studied cements agrees with the EU references values (Table 7). Only sample SPC-30-50 presents an I around 1 (cement with 50% of PG). On the other hand, the values of Ra(eq) for all cements are below the set limit of 370 Bq kg⁻¹, which is the limit considered in USA to be used the PG in any application.

3.3.2. Radon potential and exhalation rate of matrix and blocks

Radon emanation factor is the fraction of the ²²²Rn which has been produced by the ²²⁶Ra in a sample and reaches the pores of material; i.e., emanation factor is the fraction of radon produced in the material that is free to be transported through its pores. The product of radium concentration per the emanation factor is the radon potential. In Table 8 are shown the results of radon poten-

Table 7
Radium equivalent activities and the activity concentration index I of PG-SPC samples.

Code	SPC-17-10	SPC-19-20	SPC-21-30	SPC-26-40	SPC-30-50
Index "I"	0.43	0.56	0.75	0.85	1.01
Ra(eq) (Bq kg ⁻¹)	117	253	158	217	301

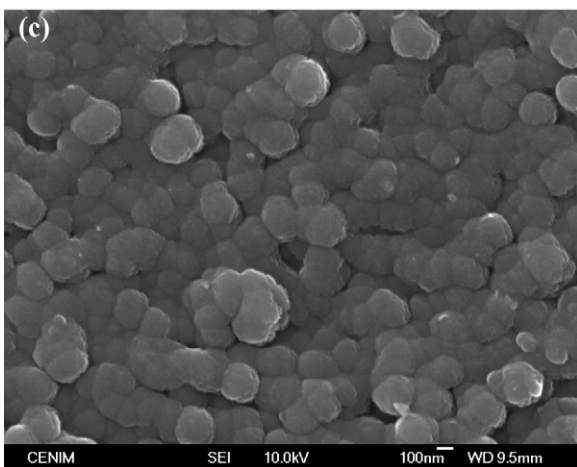
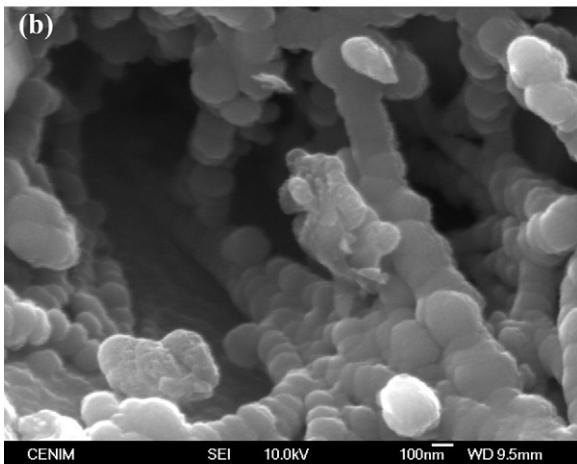
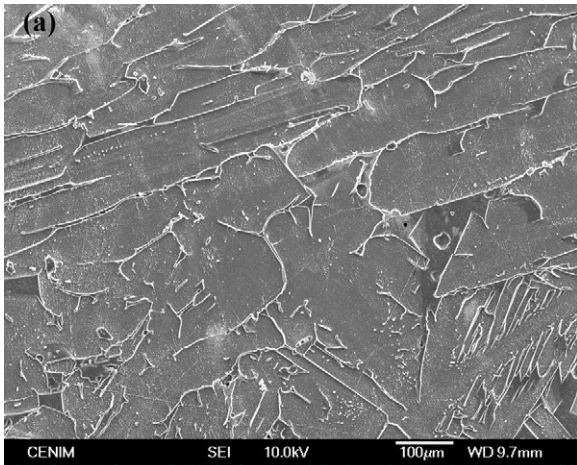


Fig. 6. SEM image of the mixture of sulfur and modified sulfur (STX®) heated at 145 °C and cooled at room temperature. (a) compact and continuous structure of a polymeric plastic material, (b) ciliated filaments and (c) micro particles of elemental sulfur (bar 150 nm).

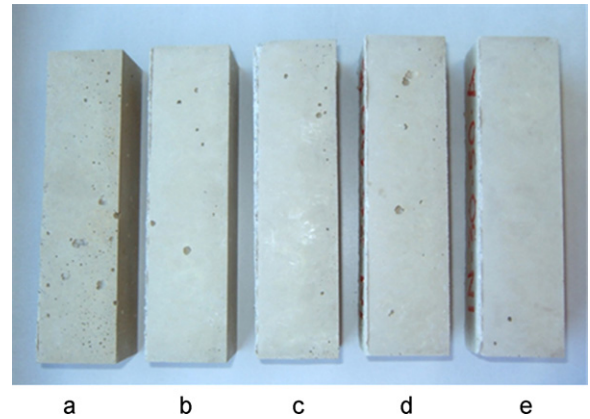


Fig. 7. Solid blocks prepared of PG-SPC (a) SPC-17-10, (b) SPC-19-20, (c) SPC-21-30, (d) SPC-26-40 and (e) SPC-30-50.

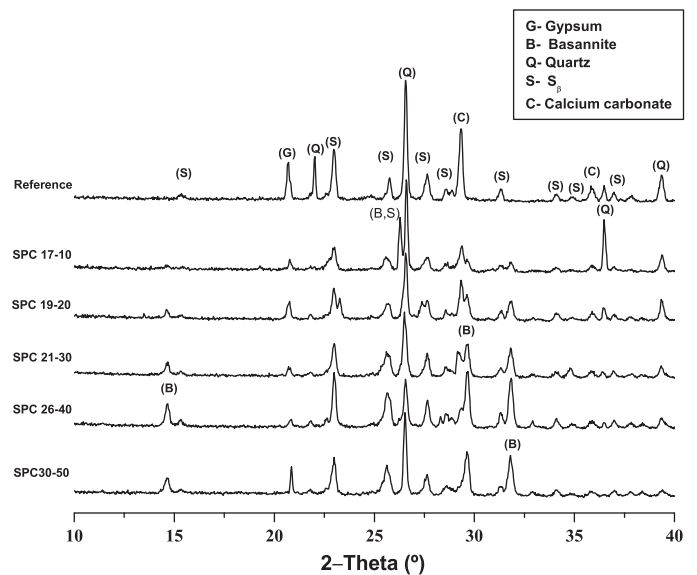


Fig. 8. XRD patterns of the SPCs samples.

tial and the emanation factor for PG and SPC in milled samples. The radon potential is a characteristic of the material that is not influenced by the experimental conditions during its determination, and then is a suitable parameter for classifying/comparing porous material in relation to its potential radon radiological risk.

Table 8
Radon potential and emanation factor of PG-SPCs and PG milled samples. (σ (Bq kg⁻¹) and Σ are their standard deviations, respectively).

Sample	Rn Pot (Bq kg ⁻¹)	σ (Bq kg ⁻¹)	Emanation factor	Σ
SPC-17-10	10.3	0.9	0.164	0.020
SPC-19-20	11.3	1.0	0.098	0.012
SPC-21-30	22.3	1.7	0.132	0.014
SPC-26-40	19.1	1.0	0.084	0.007
SPC-30-50	30.6	1.7	0.108	0.009
PG	68.4	4.2	0.116	0.011

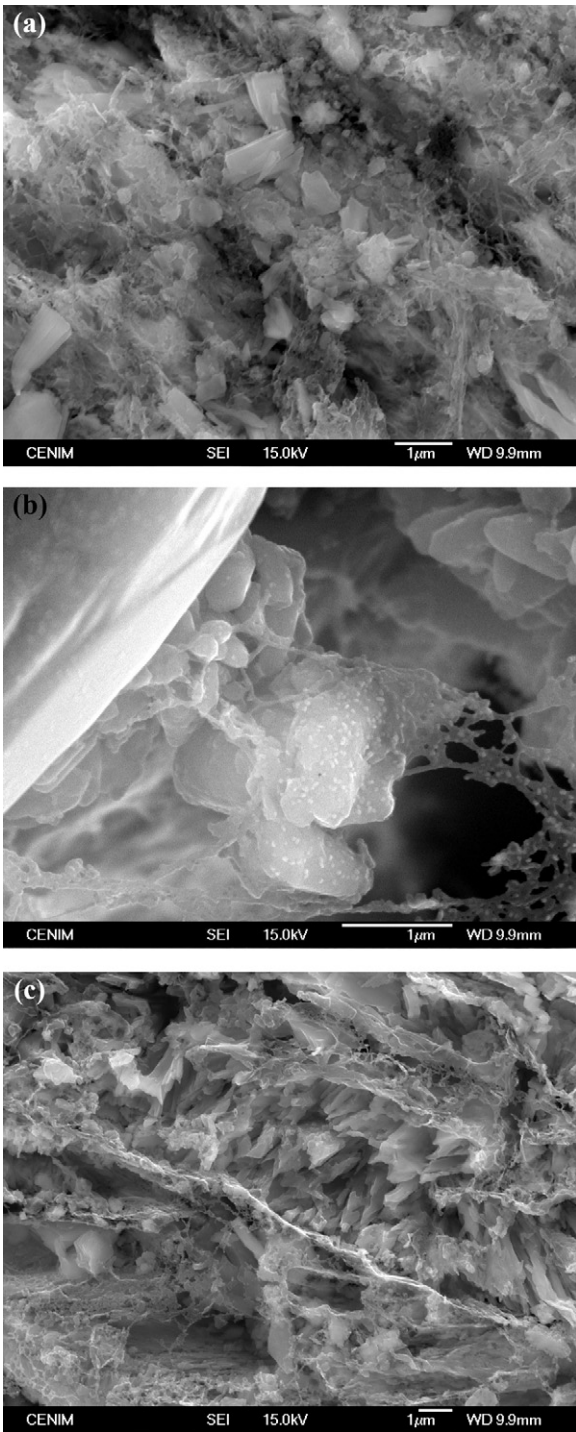


Fig. 9. SEM image of particles of PG bonding from the plasticized sulfur in the SPC-26-40 sample.

The values obtained for radon potential range from 10.3 to 30.6 Bq kg⁻¹ in SPC cements, finding the highest value (68.4 Bq kg⁻¹) for the pure PG sample, as it was expected. As general tendency, we can affirm that radon potential and emanation factors increase on the fraction of PG in the SPC sample. On the other hand, the emanation factors are very similar for all samples, including PG, with values ranging from 0.1 to 0.16.

Table 9 shows the values for radon exhalation, which are in the order of magnitude of the detection limit of the measurement system, and therefore the uncertainties associated with these measurements are relatively high. However, these measurements allow

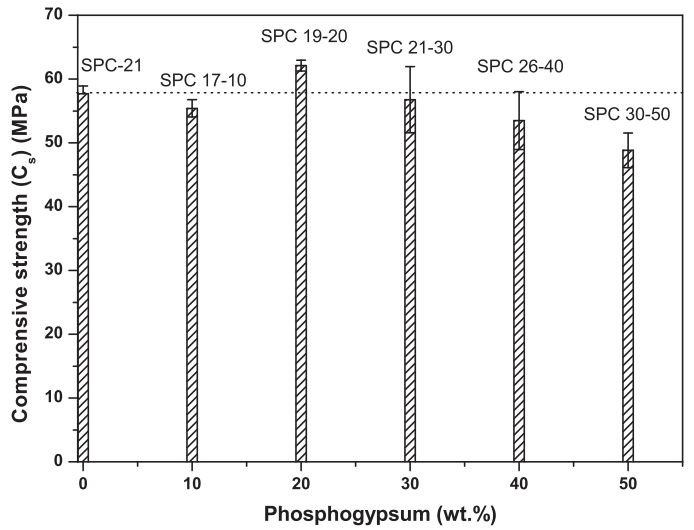


Fig. 10. Variation of compressive strength with content of PG in SPCs samples.

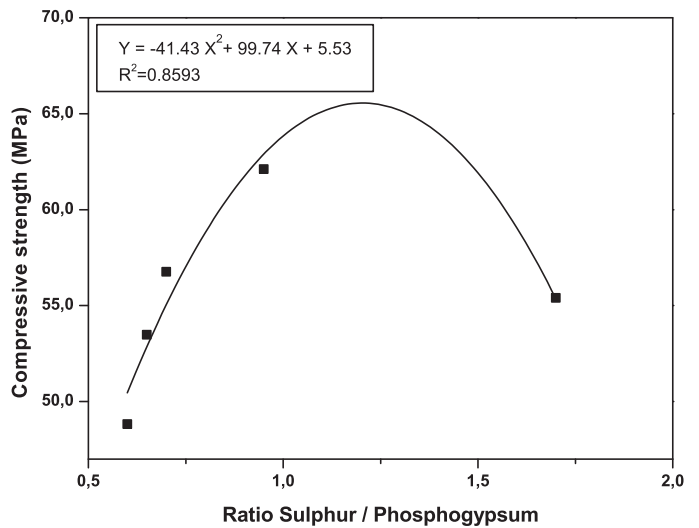


Fig. 11. Effect of sulfur to PG ratio on the compressive strength of sulfur polymer concrete.

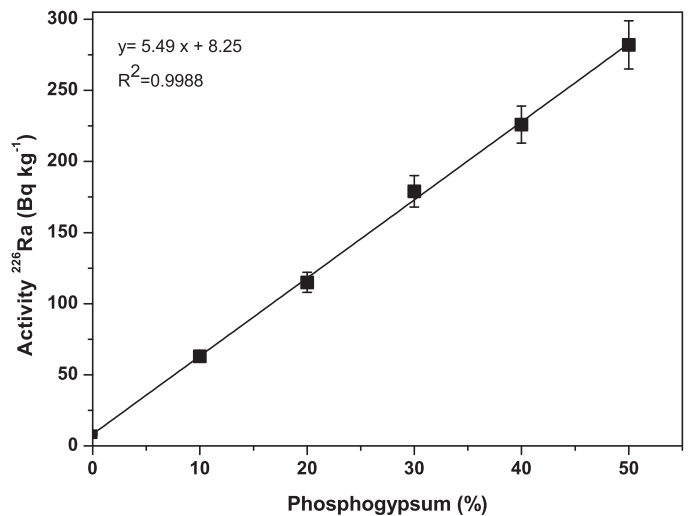


Fig. 12. Variation of activity concentration of ²²⁶Ra (Bq kg⁻¹) with content of PG in the SPC samples.

Table 9
Bulk exhalation (Eb), and diffusion coefficient (Db) calculated for blocks 160 mm × 40 mm × 40 mm.

Sample	Eb (Bq m ⁻² h ⁻¹)	σ (Bq m ⁻² h ⁻¹)	Db (m ² s ⁻¹)
SPC-17-10	1.0	3.8	4.58E-08
SPC-19-20	1.0	3.8	2.77E-08
SPC-21-30	1.4	0.9	4.24E-08
SPC-26-40	1.5	0.9	6.57E-08
SPC-30-50	1.5	1.1	1.24E-07

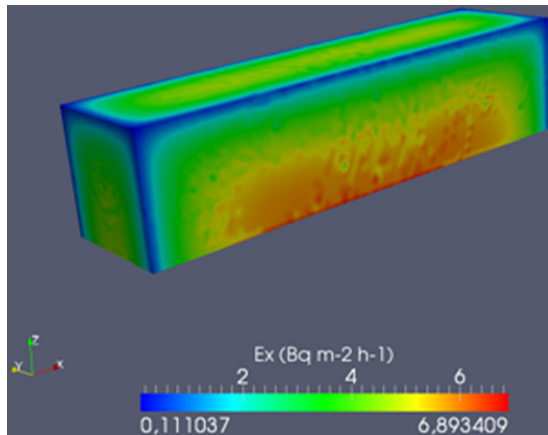


Fig. 13. Radon exhalation rate obtained by modeling a specimen of 40 mm × 40 mm × 160 mm made with SPC-30-50 sample.

us to verify the low radon exhalation rates obtained for these building materials, which in no case exceed 2 Bq m⁻² h⁻¹.

3.3.3. Simulation by modeling of exhalation rates

It has been carried out by modeling a simulation of a block of SPC cement (SPC-30-50) that emanates through all its sides excepting for the base (160 mm × 40 mm). As shown in Fig. 13, the piece does not have a radon exhalation rate uniform across all points of its surface. 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, which is very similar to the experimental value ones.

We have applied this model to different plasterboard made off SPCs cements considered in this study, finding that their exhalation rates range from 4 to 12 Bq m⁻² h⁻¹. These values are of the same order of magnitude of typical building materials, or slightly higher [49–51], which are in a typical range of 1–10 Bq m⁻² h⁻¹. The mean value for the exhalation rate of the plate made of with SPC-30-50 (assuming you exhale only one side) is 11.7 ± 1.4 Bq m⁻² h⁻¹, and being the highest values found near the edges of the plate. Thus, the central part of the plate around presents a value of 9 Bq m⁻² h⁻¹, while their edges have values until above 15 Bq m⁻² h⁻¹.

To complete the study of radon, we will analyze the obtained results for radon concentration inside a standard room (5 m × 5 m × 2 m) built with the plates shown in Table 10. During good ventilation (air enhance = λ_v = 2 h⁻¹) shows that the high-

Table 10
Radon exhalation rate of a plate of 1 m × 1 m × 0.04 m, and the expected radon concentration (C_{Rn}) in a standard room.

Sample	E (Bq m ⁻² h ⁻¹)	σ (Bq m ⁻² h ⁻¹)	C _{Rn} (Bq m ⁻³) (λ _v = 0.1 h ⁻¹)	C _{Rn} (Bq m ⁻³) (λ _v = 2 h ⁻¹)
SPC-17-10	4.0	0.5	67	4
SPC-19-20	4.4	0.5	74	4
SPC-21-30	8.7	1.1	146	8
SPC-26-40	7.5	0.9	125	7
SPC-30-50	11.7	1.4	196	10

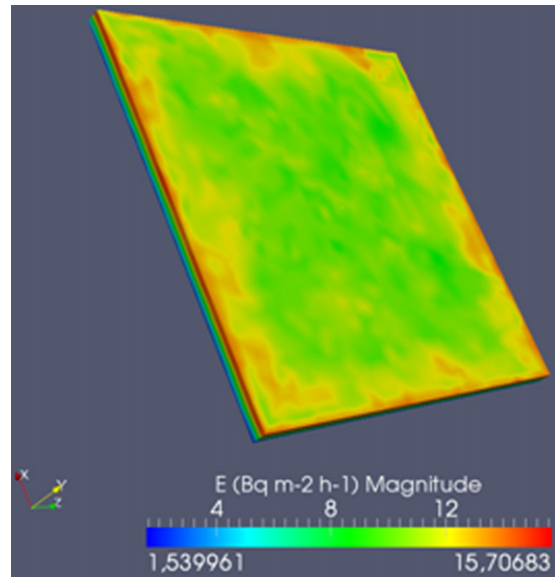


Fig. 14. Radon exhalation rates obtained for different surface points of plasterboard (1 m × 1 m × 0.04 m) of SPC-30-50 sample.

est radon concentration reached inside the room is 10 Bq m⁻³, as expected, for cement with 50% of PG (code SPC-30-50). However, under poor ventilation (λ_v = 0.1 h⁻¹) average radon concentrations up to 200 Bq m⁻³ are achieved, which is the reference value in the EU for new houses (Fig. 14).

3.4. Accelerated leach test

Table 11 shows the leach results recorded. According to Eq. (8), the reference cement (SPC-21) returned somewhat smaller absorption coefficients than the SPC-21-30 (mean values 1.07 and 1.48%, respectively). For the reference cement the pH directly influenced the value of the coefficient, with mean values of 1.3 and 0.85% calculated for the acidic and basic media, respectively. This variation was less accentuated in the SPC-21-30 sample (mean 1.79% for the acidic media and 1.17% for the basic media).

Neither ²²⁶Ra, ²³⁴Th, ²³²Th, ⁴⁰K nor ²¹⁰Pb were detected in the leachates (i.e., the concentrations were below the 1 and 3 Bq l⁻¹ detection limits), thus providing leaching coefficients of <1%. Only the results for ²³⁸U and ²¹⁰Po (which were measured using more sensitive techniques) are therefore discussed.

The mean concentrations of ²³⁸U in the reference cement (SPC-21) leachate was 0.10 Bq l⁻¹ for the acidic media, and 0.011 Bq l⁻¹ for the basic media, similar to the values recorded for inland water bodies (typical range 0.005–0.5 Bq l⁻¹) [52]. The mean leaching coefficient for ²³⁸U was 0.62% for the SPC-21-30 cement, being higher in acidic media (0.99%) than basic media (0.07%), as expected [53].

The SPC-21-30 cement leachate had a mean ²³⁸U concentration of around 1 Bq l⁻¹ in acidic media, falling to 0.62 Bq l⁻¹ for pH (2–10) media (close to the upper limits allowed for groundwater affected by mining residues [1 Bq l⁻¹]) [54,55]. The mean leaching coefficient was 0.66%, and once again higher in acidic (1.05%) than in basic media (0.07%). This, plus the results outlined in Table 11, shows that the contamination of water by uranium isotopes by SPC-21-30 cement would be negligible.

At 0.001–0.1 Bq l⁻¹, the range of concentrations recorded for ²¹⁰Po was 1–2 orders of magnitude lower than for ²³⁸U [53]. Table 11 shows that, for the reference sample, the mean activity in the acidic media was 0.028 Bq l⁻¹, below the mean 0.01 Bq l⁻¹ recorded for basic media. For SPC-21-30 cement it was somewhat

Table 11
Water absorption coefficients, ^{238}U and ^{210}Po concentrations, and leaching coefficients with respect to pH.

Sample	pH	A_c (wt.%)	^{238}U (Bq l ⁻¹)	^{210}Po (Bq l ⁻¹)	L_c ^{238}U (%)	L_c ^{210}Po (%)
Reference (SPC-21)	2	1.63	0.080 ± 0.003	<0.01	0.27	<0.01
	4	1.01	0.143 ± 0.012	0.039 ± 0.019	0.48	0.19
	6	1.25	0.078 ± 0.005	0.017 ± 0.011	0.26	0.09
	8	0.95	0.0106 ± 0.0003	<0.01	0.03	<0.01
	10	0.75	<0.01	<0.01	<0.01	<0.01
Mean for acidic media		1.30	0.10 ± 0.01	0.028 ± 0.015	0.34	0.14
Mean for basic media		0.85	0.011 ± 0.001	<0.01	0.03	<0.01
Mean (pH 2–10)		1.07	0.078 ± 0.005	0.028 ± 0.015	0.26	0.14
SPC-21-30	2	1.50	1.09 ± 0.05	0.97 ± 0.07	1.17	0.18
	4	1.89	0.73 ± 0.05	0.15 ± 0.03	0.78	0.03
	6	1.99	1.14 ± 0.04	0.067 ± 0.017	1.22	0.01
	8	1.46	0.09 ± 0.03	<0.01	0.09	<0.01
	10	0.87	0.05 ± 0.01	<0.01	0.05	<0.01
Mean for acidic media		1.79	0.99 ± 0.05	0.39 ± 0.04	1.05	0.07
Mean for basic media		1.17	0.07 ± 0.02	<0.01	0.07	<0.01
Mean (pH 2–10)		1.48	0.62 ± 0.04	0.39 ± 0.01	0.66	0.07

higher (at around levels for inland water bodies) in acidic media, but lower (0.01 Bq l⁻¹) in basic media. The leaching coefficient in the acidic media was 0.14% for SPC-21, and 0.07% for SPC-21-30.

Finally, the concentration of ^{238}U was about twice that of ^{210}Po in the leachate, in agreement with the fact that Po tends to become more strongly fixed to particulate material than U [54].

4. Conclusions

The stabilization and solidification of a phosphogypsum with low radionuclide activity using sulfur polymer cement allows the disposal of both sulfur and PG. This could help to reduce the environmental impact of PG land disposal, eliminating the potential for further contamination.

The S/S process has permitted the obtainment of PG-SPC cements with good mechanical properties. Compared to the reference samples, the mechanical properties of the PG-SPC incorporating up to 40% PG do not seem to be affected.

In relation to radiological findings, we conclude that the activity concentration index (I) in the polymer cements is lower than the reference value in most international regulations and, therefore, these cements can be used without radiological restrictions in the manufacture of building materials. On the other hand, in USA and other countries, it is often used in the radiological control of building materials the equivalent radium concentration, $Ra(\text{eq})$, finding that all the cement samples have $Ra(\text{eq})$ less than the reference value set by the EPA for construction materials (370 Bq kg⁻¹).

Furthermore, in terms of the proportion of phosphogypsum used in the mix, the potential for radon is increased, but the sulfur polymer cement shows an emanation factor always very less than the original components for its manufacturing (sulfur, gravels, phosphogypsum, etc.) because the curing process significantly reduces the radon exhalation from these materials. PG-SPCs produced cements have radon exhalation rates only slightly higher than the typical values of building materials, and considerably lower than typical values of soil exhalation. In this sense, we can affirm that under normal conditions of ventilation, the contribution to the expected radon indoor concentration is below the international recommendations for indoor radon, so the building materials studied in this work can be applied in the houses' construction under normal ventilation conditions.

According to the obtained results the water absorption capillarity (WAC) is slowly higher in SPC cements containing PG than normal SPC ones, but it is lower than the standard Ordinary Portland Cement.

Finally, accelerated leach tests showed that even the leaching coefficients in acidic media are always higher than in alkaline

solutions, either for ^{238}U or ^{210}Po , these values in both cases are always under international recommendations, thus, contamination of waters from these and other radionuclides tested can be considered negligible.

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