Preliminary studies of a phosphogypsum stabilisation process
using a sulphur polymer matrix

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Abstract

The production of phosphoric acid from natural phosphate rock by means of the wet process gives rise to an industrial by-product named phosphogypsum (PG). World PG generation is estimated to be around 100-280 million tonnes/year. PG is mainly composed of gypsum but also contains a high level of impurities such as phosphates, fluorides, naturally occurring radionuclides, heavy metals, and other trace elements. All of this adds up to a negative environmental impact and many restrictions on PG applications. PG is disposed of without any treatment, usually by dumping in large stockpiles that occupy considerable land areas and cause serious environmental damage, particularly in coastal regions. The USEPA has classified PG as a “Technologically Enhanced Naturally Occurring Radioactive Material” (TENORM).

This paper reports a proposed PG stabilisation/solidification (S/S) process by means of sulphur polymer concrete. Final products have been obtained in the form of standard monoliths. Mechanical properties (compressive and flexural strength) have been studied and radionuclide contents determined. Results show the obtainment of sulphur and phosphogypsum concretes with good mechanical properties and low radionuclide contents. The PG S/S process can thus be considered a very suitable and efficient option for PG disposal.

Key words: phosphogypsum, radionuclides, sulphur polymer concrete, stabilisation/solidification, TENORM.
1. Introduction

Phosphogypsum (PG) is a waste by-product from processing phosphate rock by the "wet acid" method for phosphoric acid production in fertiliser plants. This process is economic but results in the production of a large amount of PG [1]. About 5 tonnes of PG are generated for every tonne of phosphoric acid produced [2]. World PG production is variously estimated to be in the region of 100-280 Mt per year [3]. In the wet process the phosphate content of the rock is converted by concentrated sulphuric acid to phosphoric acid and a calcium sulphate residue in either dihydrate (CaSO$_4$·2H$_2$O) or hemihydrate form (CaSO$_4$·1/2H$_2$O) (Eq. 1):

$$[\text{Ca}_3(\text{PO}_4)_2]_3\text{CaF}_2+10\text{H}_2\text{SO}_4+n\text{H}_2\text{O} \rightarrow 6\text{H}_3\text{PO}_4+10(\text{CaSO}_4 \cdot n\text{H}_2\text{O}) +2\text{HF} \quad (1)$$

Phosphate ore \hspace{2cm} phosphogypsum

$n = \frac{1}{2} \rightarrow$ hemihydrate (CaSO$_4$, $\frac{1}{2}$ H$_2$O)

$n = 2 \rightarrow$ dihydrate (CaSO$_4$, 2 H$_2$O)

PG is mainly CaSO$_4$·2H$_2$O but also contains impurities such as free phosphoric acid, phosphates, fluorides and organic matter that adhere to the surface of the gypsum crystals [4]. Previous studies have focused on reducing impurity levels in PG [5-8]. Heat treatment has been mostly used to obtain an anhydrite phase for use in building and road construction materials [9-12].

PG is one of the most serious problems facing the phosphate industry, since only 15% of the world production is recycled as an agricultural fertiliser, a building material or a soil stabilisation amendment [13, 14]. The remaining 85% of PG is dumped in the
vicinity of phosphate factories, requiring large disposal areas. PG dumping causes soil, water and air pollution. The main problems associated with the accumulation of PG without any treatment are the relatively high levels of natural uranium-series radionuclides and the leacheability of hazardous elements. Previous study performed by Bolivar et al. (2000) [15] showed that about 80% of the $^{226}$Ra, 90% of the $^{210}$Po and 20% of the $^{238}$U and $^{234}$U originally present in the phosphate rock remain in PG. Researchers have reported a wide variety of radionuclide concentrations in different PG sources (Table 1) [16-18]. The data shows that all the different PG sources were low in $^{238}$U and that $^{226}$Ra and $^{210}$Po constituted the most important radioactivity sources. The United States Environmental Protection Agency (EPA) [2] has classified PG as a “Technologically Enhanced Naturally Occurring Radioactive Material” (TENORM), and since 1992 has banned PG with a radioactivity exceeding 370 Bq kg$^{-1}$ (10 pCi g$^{-1}$) for any use. Nevertheless, there is no unanimity on the “safe limit” for radioactive exposure due to PG. In the meanwhile, the phosphate industry has been looking for different ways to reduce the size of PG stacks.

Stabilisation/solidification (S/S) technologies have successfully been used for many years to immobilise hazardous wastes. In 1987 the EPA defined S/S technologies as BDATs (Best Demonstrated and Available Technologies). In the literature S/S procedures for PG using cement, fly ash and lime are widely described and especially focused on the manufacture of solids monoliths with suitable mechanical properties to ensure better handling and prevent the leacheability and migration of hazardous elements [19] and for widescale application in building industries [9-12, 20-24]. However, attention has scarcely been paid to discussing the management and inertisation of the natural radionuclides present in raw PG [25].
The increase in environmental restrictions on fuels in recent decades has led to the generation of large amounts of sulphur waste throughout the world, making it necessary to develop new applications for this element. As a result, “sulphur cement” was obtained by mixing 95% of elemental sulphur (a residue of the oil industry) with 5% of sulphur modified with organic compounds, normally obtained from petroleum refining (ciclopentadienile and its derivatives) [26]. This mixture melted at about 160 ºC is added to conventional gravel and sand to form Sulphur Polymer Concrete (SPC) [27, 28]. SPC has been one of the most interesting developments in the last twenty years, due to the relative simplicity of its manufacturing and its interesting properties. Compared to ordinary Portland cement, SPC displays better hydraulic and mechanical properties and higher chemical and corrosion resistance. Moreover, SPC properties are not affected by presence of salts, acids or bases [29]. Therefore, several researchers have addressed the use of SPC for the inertisation and encapsulation of radioactive residues [30-32].

The EU LIFE-MERSADE project has recently developed safe storage methods for mercury. One of the studied methods, based on the immobilisation of Hg in a sulphur matrix (similar to that used in this study), has yielded excellent results [33].

The main objective of this work is to perform preliminary study with the aim of evaluating the possibility of confining the radionuclides contained in a low activity PG (with low levels of natural radionuclides) in a matrix obtained by polymerisation with sulphur using the S/S process. The natural radionuclides content was determined before and after the treatment and the mechanical behaviour of the monoliths obtained in the form of 160 x 40 x 40 mm standard monoliths was studied.
2. Experimental Procedure

2.1. Materials

The PG used in this study came from a fertiliser factory in Sfax city, Tunisia. Granular sulphur type Rubber Sul 10 with a grain size of less than 60 µm from REPSOL IPF refineries (Madrid, Spain) and modified sulphur (sulphur-containing polymer) STX™ supplied by Starcrete™ Technologies Inc. (Québec, Canada) were employed.

Two types of samples were prepared: T1 reference samples (SPC) without PG addition and T2 samples containing PG (SPC-PG). The SPC samples were prepared using a mixture of gravel with a grain size of less than 6.3 mm, silica sand in a proportion of 0.43 wt% and calcium carbonate (99.5% purity, Panreac) as filler (10% of the mixture). The SPC-PG samples were manufactured similarly to the SPC samples, but in this case, instead of the filler (calcium carbonate) the same amount of PG was added to the mixture. Different sulphur percentages were tested in both samples (15 and 17%).

2.2. Preparation of samples (SPC and SPC-PG)

The grain size distribution of the different aggregates used in the preparation of the different samples was designed according to the Spanish prescription for concrete [34]. The SPC and SPC-PG samples were prepared according to the procedure described by Vromm [28] and STARTcrete™ Technologies Inc. [35]. The previously preheated mixture of gravel, filler and sulphur was stirred in an IBERTEST Mod. 16-
L005B mixer, provided with a temperature control system, for about 30 min until reaching 145 °C. At this temperature the elemental sulphur was already molten and the modifier sulphur STX™ was added. Temperature control is very important at this stage because at temperatures above 150 °C the viscosity can increase rapidly, causing poor workability and handling of the mixtures. The sulphur content also influences the workability of the mixture, so the samples with 17% sulphur showed better workability than those with 15%.

The mixtures were homogenised in the mixer and then poured into preheated standard moulds (160 x 40 x 40 mm) (UNE 102031-99) [36] and compacted by a vibrating table at 3000 rpm for 30-60 seconds (depending on the sample viscosity). The samples were then air-cooled to room temperature, demolded and stored until further analysis.

Fig.1 shows a comparative view of the obtained monoliths (SPC and SPC-PG) and Table 2 reports the composition (wt%) of the different samples.

2.3. Sample characterisation

The semiquantitative chemical composition of the PG samples shown in Table 3 was identified by an X-ray fluorescence analyser (Philips model PW-1404 sequential wavelength dispersion unit). Mineral species were determined by X-ray diffraction (Siemens model D5000, with a Cu tube and LiF monochromator).

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were performed using a Setaram SETSYS Evolution (Model 1500) equipment. DTA/TG curves were obtained by heating a 36 mg PG sample in an argon atmosphere (20
ml/min) and using alumina crucibles at a heating rate of 20°C/min. The DTA/TG signal curves were measured and integrated by means of Setaram Setsoft 2000 software.

Mechanical properties were determined according to the standard test procedure (UNE 102031, 1999) [36]. Compressive and flexural tests were carried out using Ibertest model Autotest-200/SWC equipment, scale: 10 KN, rate: 0.05 KN/s and 2.4 KN/s for flexural and compressive strengths, respectively. Three monoliths were used for each sample test in order to get an average value. For each monolith, 1 value for flexural strength and 2 values for compressive strength were obtained.

The morphological and microstructural aspect of the raw PG and the stabilised samples (SPC-PG) were analysed using scanning electron microscopy (SEM) (Joel model JXA-840) with energy dispersive spectroscopy (EDS) on the surface fracture resulting from flexural strength.

2.4 Analysis of natural radionuclides

Natural selected radionuclides belonging to uranium and thorium decay series and $^{40}$K have been quantified in both phosphogypsum (PG) and concrete stabilised PG (SPC-PG) samples.

Uranium

The total uranium concentration was determined using two measuring techniques: i) gamma spectrometry with high-purity germanium detectors and ii) laser-induced kinetic phosphorimetry (KPA-11 Chemcheck Instruments Inc., Richland, WA) [37]. Direct measurements by gamma spectrometry were carried out on 700-g aliquots of the samples packed in standard marinelli beakers. The $^{238}$U activity concentration was determined through the photopeaks of its daughter, $^{234}$Th (63 and 92.5 keV), whereas
$^{235}\text{U}$ was measured directly from its 143.8 keV gamma ray peak. Measurement by laser-induced kinetic phosphorimetry requires complete dissolution of the sample. Different mixtures of acids were used depending on the sample matrix. 1 g of the SPC-PG sample was totally dissolved by microwave digestion, using a mixture of HNO$_3$/HF/HCl acids. The same quantity (1 g) was used for the PG sample, being digested in 15.6 mol·l$^{-1}$ HNO$_3$. With this measuring technique the resulting concentration refers to total uranium and is expressed in µg·g$^{-1}$. In order to compare the results obtained by both techniques it is necessary to convert this value to the activity concentration of each uranium isotope. Theoretical values of the isotopic composition of natural uranium (99.3% $^{238}\text{U}$, 0.72% $^{235}\text{U}$, and 5.5·10$^{-3}$ % $^{234}\text{U}$) and the specific activity of these uranium isotopes (Bq·g$^{-1}$) were used for this purpose [38].

$^{210}\text{Po}$

The polonium activity concentration was determined by alpha spectrometry. An aliquot of 1 g was digested in a hot plate at a controlled temperature (<90 ºC), using 8 mol·l$^{-1}$ HNO$_3$ for PG samples and a mixture of HNO$_3$/HF/HCl for SPC-PG samples. $^{209}\text{Po}$ standard dissolution was added to the dissolved samples as a tracer to estimate the recovery of the whole process. The polonium isotopes were self-deposited on silver disks following Flynn’s method [39].

$^{226}\text{Ra}$, $^{232}\text{Th}$, $^{210}\text{Pb}$ and $^{40}\text{K}$

These radionuclides were analysed by gamma spectrometry using the same geometry described above, with standard marinelli beakers. The samples were packed, hermetically sealed and stored for about four weeks prior to counting so as to ensure radioactive equilibrium between $^{226}\text{Ra}$ and its short lived progeny. $^{226}\text{Ra}$ and $^{232}\text{Th}$ were determined through the photopeaks of their daughters, $^{214}\text{Bi}$ (609 keV) and $^{228}\text{Ac}$ (911.2
keV, 969.0 keV) respectively. $^{210}$Pb and $^{40}$K were measured directly from their gamma ray peaks, 46.5 keV and 1460.8 keV respectively.

3. Results and discussion

3.1. Characterisation of phosphogypsum

The chemical composition of the PG sample is summarised in Table 3. The data shows that sulphate (expressed as SO$_3$), CaO, F, SiO$_2$ and P$_2$O$_5$ are the major compounds. The powder X-ray diffraction pattern of PG is reported in Fig. 2. As shown, the main diffraction peak corresponds to gypsum (CaSO$_4$.2H$_2$O) (JCPDS 33-0311). The pH value of PG was 3.2 as a consequence of the residual phosphoric acid and sulphuric acid contained within the pores of the gypsum grains or adhered to their surface.

Fig. 3 illustrates the DTA/TGA curve of PG. The DTA curve (Fig. 3a) is characteristic of the thermal decomposition of gypsum and is in concordance with the results obtained by XRD. The first endothermic effect observed at 64 ºC is associated to partial dehydration to form bassanite, according to Eq. 3:

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O}$$

Gypsum       Bassanite

The second endothermic effect takes place at 158 ºC as a consequence of dehydration of the hemihydrate and consequently the formation of soluble anhydrite III, according to Eq. 4:
CaSO₄, ½ H₂O → CaSO₄ + ½ H₂O \hspace{2cm} (4)

\text{Bassanite} \hspace{1cm} \text{Anhydrite III}

The exothermic peak observed at 457 °C, which is not associated with any mass loss, corresponds to the transformation of soluble anhydrite III to insoluble anhydrite II (Eq. 5):

\text{CaSO₄ III} \rightarrow \text{CaSO₄ II} \hspace{2cm} (5)

\text{Anhydrite III} \hspace{1cm} \text{Anhydrite II}

At 1175.2 °C a small endothermic signal is observed which corresponds to the transformation of anhydrite II to anhydrite I, according to Eq. 6:

\text{CaSO₄ II} \rightarrow \text{CaSO₄ I} \hspace{2cm} (6)

\text{Anhydrite II} \hspace{1cm} \text{Anhydrite I}

This last effect precedes the decomposition of calcium sulphate, which takes place at 1204 °C according to Eq. 7 and appears clearly in the DTA curve as a relevant endothermic peak.

\text{CaSO₄ I} \rightarrow \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \hspace{2cm} (7)
The DTA curve shows other endothermic signals at 1098 °C and 1288.1 °C which may be attributed to the decomposition of carbonates, CO₂ emissions and other impurities previously present in the PG.

On the other hand, the TGA curve (Fig. 3b) shows an initial mass loss at 64 °C. This effect is due to the elimination of \( \frac{1}{2} \) H₂O as mentioned above. The second mass loss of 18.1% seen between 92 °C and 399 °C corresponds to the complete removal of crystallisation water.

No mass loss was observed between 400 °C and 500 °C, but from 500 °C to 1100 °C a mass loss of 0.9% occurred, which is attributed to the removal of CO₂ as a consequence of thermal decomposition of some carbonate associated to the PG. Finally, a mass loss of 10.7% takes place between 1100 °C and 1300 °C, which corresponds to the decomposition of CaSO₄. The total mass loss up to 1300 °C is 29.7%. These results are concordant with those obtained by Sebbahi et al. (1997) [40] on the thermal behaviour of Moroccan phosphogypsum and also with the data reported by Hudson-Lamb et al. (1996) [41] on the thermal decomposition of natural gypsum and pure calcium sulphate.

3.2. Mechanical properties of samples

The results of the mechanical properties study (Table 4) show that the incorporation of PG as filler instead of calcium carbonate does not cause any significant variation in flexural strength values compared to the reference samples, while the compressive strength values decrease slightly. Moreover, the mechanical behaviour of the samples does not seem to be affected by increasing the amount of sulphur in the
mixture, although the data shows slightly lower flexural strength values for both the reference (SPC) and PG (SPC-PG) samples with a sulphur content of 17% wt.

3.3 Morphological study

The morphological structure of untreated PG, as determined by SEM, is illustrated in Fig. 4, which shows two different sections of the sample. The micrographs reveal a homogeneous and prismatic PG piling arrangement and a well-defined crystalline structure with a majority of orthorhombic shaped crystals. Miloš et al., 2003 [42], explained that this PG marked crystal structure indicates that PG presents a more complex composition than natural gypsum (characterised by a poorly expressed crystalline structure), which may eventually influence its chemical behaviour.

On the other hand, the fracture surface of the SPC-PG17 monolith was studied by SEM and the element concentrations were measured using energy dispersive analysis. The obtained micrographs are illustrated in Fig. 5. As general characteristics, the sample presents a porous structure (Fig. 5a and b). Needle-like crystals partly cover the surface of the sample (Fig. 5b and c) and are also very developed in the pores (Fig. 5c). As shown in the micrograph (Fig. 5d), different kinds of sulphur crystal sizes can be appreciated. Moreover, Fig. 5d reveals an unusual phenomenon of ordered angular crystallisation. In the areas where there are pores, the sulphur develops fibrous and crystalline structures of a considerable size and the ciliated fibres project from each crystal into the matrix [43], which is considered a typical example of sulphur crystal growth. Sulphur thus seems to cover and bond the PG grain and aggregates (sand and gravel) and also to fill the inner spaces, improving microstructural continuity and thereby improving mechanical properties.
3.4 Natural radionuclides levels

The activity concentration results obtained by the two techniques employed for this purpose are reported in Tables 5 and 6.

The sensitivity of the analytical methods is good enough to detect the radionuclides existing in both types of samples: PG and SPC-PG. The use of gamma spectrometry for uranium determination allows the analysis of a more representative aliquot of the whole sample than in the case of the KPA technique. KPA has a lower detection limit (sensitivity) and better uncertainty (6%), but due to the limitations of wet digestion until total dissolution and chemical interferences, only 1 g can be analysed. Nevertheless, the results obtained from both techniques are in good agreement (Table 5) and they report adequate values for the goals of this study.

Attention is drawn to the low natural radionuclide levels present in the PG samples from Tunisia (30.7 Bq·kg⁻¹ average value for $^{238}$U, 188 Bq·kg⁻¹($^{226}$Ra), 194 Bq·kg⁻¹($^{210}$Po), 12.4 Bq·kg⁻¹($^{232}$Th) and 13 Bq·kg⁻¹($^{40}$K)) compared to the levels of PG samples from other world regions (Table 1) and Spain (Table 7) [44]. This different content may be attributed to the natural radionuclide concentration in the raw material and differences in the industrial process applied to obtain phosphoric acid. Natural radioactivity in the different phases of the production system has recently been analysed by Bolivar et al., 2009 [45], showing that Pb, Ra and to a certain extent Th isotopes are exclusively supplied by the phosphate rock and remain associated to the phosphogypsum particles, while uranium decreases according to the number of washings of the PG.
In the materials stabilised with sulphur, SPC-PG (15-17), with a PG content above 8% wt, the natural radionuclide concentration is lower than that determined in the initial PG (Table 6). This decrease is obvious, as the percentage of natural radionuclides determined in the SPC-PG is in good accordance with the amount of PG used in its preparation (approx. 8%), except in the cases of $^{40}$K, $^{232}$Th and $^{238}$U. $^{40}$K could be added via another component (sulphur or polymer) of the SPC-PG, and uranium and thorium are likely natural components of the gravel, therefore increasing the content of these radionuclides in the SPC-PG samples. Recent studies of gravel show concentrations of $18.8 \pm 5.5$ Bq·kg$^{-1}$ ($^{238}$U) and $14.8 \pm 1.8$ Bq·kg$^{-1}$ ($^{232}$Th), which would indicate that activity concentrations would be higher than those expected according to the dilution factor in the mixture.

Having determined the physical and mechanical properties of the SPC-PG, the natural radioactivity levels of these products were compared to those present in commercial cements used as building materials. Papaeftymiou and Gouseti, (2008) [46] in an extensive study on natural radioactivity and associated radiation hazards in buildings in Greece, quantified the concentration of $^{226}$Ra, $^{232}$Th and $^{40}$K in various materials: Pozzolanic and Portland cements, limestone, white cement, marble powder and sand, and collect worldwide values. Our concentration levels for these elements are within the world ranges for building materials and lower than those obtained in soils (17–60) Bq·kg$^{-1}$ ($^{226}$Ra) (11–64) Bq·kg$^{-1}$ ($^{232}$Th) and (140–850) Bq·kg$^{-1}$ ($^{40}$K). This means that this SPC-PG cement could be used as a building material, as the natural radioactivity level is low enough to assure an acceptable annual effective dose for a member of the public. It is also a way of recycling the PG stored in stacks close to phosphoric acid factories [44].
5. Conclusions

The stabilisation and solidification of a phosphogypsum with low radionuclide activity using sulphur polymer concrete allows the disposal of both sulphur 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 monoliths with good mechanical properties. Compared to the reference samples, the mechanical properties of the monoliths incorporating up to 10% PG do not seem to be affected.

Determination of the natural radionuclide content before and after the treatment indicates that the S/S process allows a considerable reduction of the radionuclide content in the stabilised materials.

In general terms, the results obtained are promising and may help to improve the performance and understanding of the radionuclide immobilisation process, with a view to increasing the PG content in SPC-PG samples and extending the application of this procedure to PG with a higher radionuclide activity.
Acknowledgements

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Figure legends

Fig. 1. Macroscopic aspects of the obtained prismatic monoliths: (a) SPC-series and (b) SPC-PG-series.

Fig. 2. X-ray pattern of phosphogypsum. Intensities in arbitrary units (a.u.).

Fig. 3. Thermal analysis of phosphogypsum: (a) DTA curve and (b) TGA curve.

Fig. 4. SEM micrograph of two different sections of a PG sample (15 keV).

Fig. 5. SEM micrograph of the SPC-PG17 sample fracture surface at different magnifications.
Table 1.
Radiochemical results, expressed in Bq kg\(^{-1}\), of different types of PG samples analysed [16-18].

<table>
<thead>
<tr>
<th>Origen</th>
<th>(^{238})U</th>
<th>(^{226})Ra</th>
<th>(^{210})Pb</th>
<th>(^{210})Po</th>
<th>(^{230})Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spain [16]</td>
<td>140</td>
<td>620</td>
<td>82</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>China [17]</td>
<td>15</td>
<td>85</td>
<td>82</td>
<td>82</td>
<td>-</td>
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<tr>
<td>Indonesia [17]</td>
<td>43</td>
<td>473</td>
<td>480</td>
<td>450</td>
<td>-</td>
</tr>
<tr>
<td>India [17]</td>
<td>60</td>
<td>510</td>
<td>490</td>
<td>420</td>
<td>-</td>
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<tr>
<td>Egypt [17]</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>445</td>
<td>-</td>
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<tr>
<td>Florida [18]</td>
<td>130</td>
<td>1140</td>
<td>1370</td>
<td>1030</td>
<td>113</td>
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<tr>
<td>Australia [18]</td>
<td>10</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sweden [18]</td>
<td>390</td>
<td>15</td>
<td>-</td>
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</table>
Table 2. Composition of the different SPC and SPC-PG samples expressed in wt%.

<table>
<thead>
<tr>
<th>Components</th>
<th>SPC-15</th>
<th>SPC-17</th>
<th>Sample</th>
<th>SPC-PG15</th>
<th>SPC-PG17</th>
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<tr>
<td>Gravel</td>
<td>25.0</td>
<td>24.4</td>
<td>SPC-PG15</td>
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<td>24.4</td>
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<td>Silica sand</td>
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<td>48.8</td>
<td>SPC-PG15</td>
<td>50.1</td>
<td>48.8</td>
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<td>Calcium carbonate</td>
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<td>0</td>
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<tr>
<td>PG</td>
<td>0</td>
<td>0</td>
<td>8.4</td>
<td>8.1</td>
<td>8.1</td>
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<tr>
<td>Elemental sulphur</td>
<td>15.0</td>
<td>17.0</td>
<td>15.0</td>
<td>17.0</td>
<td>17.0</td>
</tr>
<tr>
<td>STX&lt;sup&gt;MT&lt;/sup&gt;</td>
<td>1.5</td>
<td>1.7</td>
<td>1.5</td>
<td>1.7</td>
<td>1.7</td>
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Table 3.
Major element composition (wt%) of PG.

<table>
<thead>
<tr>
<th>Element</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>F⁻</th>
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<tr>
<td>Wt %</td>
<td>41.24</td>
<td>1.38</td>
<td>0.11</td>
<td>0.09</td>
<td>0.02</td>
<td>50.74</td>
<td>0.59</td>
<td>1.2</td>
<td>4.91</td>
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Table 4.
Results of mechanical properties (compressive ($C_S$) and flexural ($F_S$) strength) of monoliths: SCP-series and SPC-PG-series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_S$ (N.mm$^{-2}$)</th>
<th>$F_S$ (N.mm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC-15</td>
<td>9.6 ± 0.5</td>
<td>58.0 ± 2.7</td>
</tr>
<tr>
<td>SPC-17</td>
<td>9.3 ± 0.2</td>
<td>56.3 ± 2.3</td>
</tr>
<tr>
<td>SPC-PG15</td>
<td>9.0 ± 0.8</td>
<td>56.2 ± 2.2</td>
</tr>
<tr>
<td>SPC-PG17</td>
<td>10.0 ± 0.8</td>
<td>55.6 ± 4.6</td>
</tr>
</tbody>
</table>
Table 5.
Uranium activity ratio in the initial PG and stabilised materials, expressed in Bq·kg\(^{-1}\) (± 2s), by means of phosphorimetry and gamma spectrometry techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U (Phosphorimetry)</th>
<th>U (Gamma spectrometry) (DL)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>238(^{\text{U}})</td>
<td>234(^{\text{U}})</td>
</tr>
<tr>
<td>PG-1</td>
<td>30.4</td>
<td>31.3</td>
</tr>
<tr>
<td>PG-2</td>
<td>30.9</td>
<td>31.9</td>
</tr>
<tr>
<td>Average value</td>
<td>30.7</td>
<td>31.6</td>
</tr>
<tr>
<td>SPC-PG 15</td>
<td>14.3</td>
<td>14.7</td>
</tr>
<tr>
<td>SPC-PG 17</td>
<td>9.1</td>
<td>9.4</td>
</tr>
</tbody>
</table>

DL. Detection Limit
Tabla 6.
Natural radionuclide activity ratio of the $^{238}$Uranium-series ($^{226}$Ra, $^{210}$Pb and $^{210}$Po in this case in radioactive equilibrium), $^{232}$Th and $^{40}$K expressed in Bq·kg$^{-1}$ (± 2s) in the initial PG and stabilised materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{226}$Ra($^{214}$Bi)</th>
<th>$^{210}$Pb**</th>
<th>$^{210}$Po</th>
<th>$^{40}$K</th>
<th>$^{232}$Th($^{228}$Ac)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG-1</td>
<td>205 ± 8</td>
<td>161 ± 66</td>
<td>214± 90</td>
<td>&lt; 14</td>
<td>18.6 ± 1.4</td>
</tr>
<tr>
<td>PG-2</td>
<td>170 ± 11</td>
<td>165 ± 97</td>
<td>174±66</td>
<td>13.2 ± 5.5</td>
<td>6.3 ± 1.4</td>
</tr>
<tr>
<td>Average value</td>
<td>188 ± 9.5</td>
<td>163 ± 81</td>
<td>194 ± 78</td>
<td>&lt; 13.5</td>
<td>12.4 ± 1.4</td>
</tr>
<tr>
<td>SPC-PG 15</td>
<td>26.5 ± 2.2</td>
<td>34 ± 16 (36)*</td>
<td>25 ± 11</td>
<td>613 ± 32</td>
<td>13.3 ± 2.9</td>
</tr>
<tr>
<td>SPC-PG 17</td>
<td>27.1 ± 2.2</td>
<td>23 ± 26 (56)*</td>
<td>21 ± 10</td>
<td>730 ± 180</td>
<td>16.9 ± 2.7</td>
</tr>
</tbody>
</table>

* DL. Detection Limit
Tabla 7.
Natural radionuclide concentrations expressed in Bq·kg⁻¹ in phosphogypsum samples collected from Huelva stacks [44].

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