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Valorisation of Two Inorganic Industrial Wastes for Manufacturing Sulphur Polymer Concrete

Irene Garcia-Diaz*[,a], Felix A. Lopez[a], Francisco J. Alguacil[a], Juan P.Bolivar[b], Manuel Gazquez[b]

[a]National Center for Metallurgical Research, CENIM, CSIC, Avda. Gregorio del Amo, 8, 28040 Madrid, Spain
[b]Universidad de Huelva, Campus de El Carmen, 21071 Huelva, Spain
irenegd@cenim.csic.es

The aim of this work is the valorisation in the sulphur polymer concrete (SPC) of two hazardous wastes, phosphogypsum (PG) and non-dissolved ilmenite mud (MD), disposed in controlled disposal areas, to be utilized in the manufacture of building materials. The advantages of SPC over Portland cement concrete are quick hardening and reaching the required characteristics in only 24 h; very low water permeability; exceptional resistance to acid and salt agents, which allows its use in extremely aggressive environments. This material also allows the utilization of large amounts of sulphur from worldwide oil refineries and metallurgical industries and also SPC are stabilizing agent for various wastes. Physico-chemical characterization was performed in the wastes and in sulphur polymer concretes obtained. The optimal mixture of the materials was obtained, the solidified material have a sulfur/phosphogypsum ratio of 1:0.9 and sulphur/mud of 1:1 with a waste dosage between 10 and 30 % wt. This SPC presents highest strength between 55 to 62 MPa to SPC-PG and 36 to 64 MPa to SPC-MD and low total porosity between 2.7 and 5.0 cm^3g^{-1}. The water absorption capillarity in the samples is smaller than in conventional Portland cement.

1. Introduction

All industrial process involving minerals as raw materials are associated to the generation of inorganic hazardous wastes. In this sense, the recycling, or valorisation, of these waste generated is a research field of high interest because of the minimization of disposal, avoiding its potential release into the environment, can generate environmental and economical benefits for these industries and the general population (Shen et al. 2007). One potential use highly developed, for certain industrial wastes, is their incorporation in materials used in civil engineering, from the design phase of buildings, and even in the manufacturing of different components of these buildings (Puertas et al. 2008).
So this paper is focused on the valorisation of two hazardous waste; phosphogypsum (PG) and non-dissolved ilmenite mud (MD), with the objective to be used in the manufacture of sulfur polymer cement (SPC). These wastes are generated in NORM (Naturally Occurring Radioactive Materials) industry. In this sense, we can say that phosphogypsum and non-dissolved ilmenite mud present enhanced levels of radionuclides from the natural uranium and thorium series.
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 as As, Cd or Sr, and natural radionuclides from ^{238}U decay-series, in secular equilibrium, which are about 50 times higher than the ones in typical soils (Perez-López et al. 2010). During the industrial process a fractionation of radioelements contained in phosphate rocks is produced. In the factory of Huelva (Southwestern Spain), ^{226}Ra remains in PG (practically 100 %), ^{210}Pb - ^{210}Po (about 90 %), and ^{230}Th (70 %) (Tayibi et al.2011 a). Also, PG contains several impurities that can vary greatly depending on the source of the phos-phate rock used (Bolivar et al. 2009).
Nowadays a number of researches are focused on the search of different uses of PG – e.g. (Garg et al. 2010) for dye industries and (Coruh and Ergun 2010) for zinc leach residue waste. But only the 15 % of

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the worldwide PG production is recycled (Tayibi et al., 2009). The remaining 85 % of the PG is deposited without any treatment in regulated stacks, may pose a negative impact on the environment.
On the other hand recent studies has been obtained that the non-dissolved ilmenite mud, a waste of the titanium dioxide industry to product titanium dioxide pigment, contains a high concentration of radionuclides, greater than 1 Bq/g and it is important not forget that this waste coming from NORM industry (Gázquez et al. 2011). Until now, this mud has been disposed of in a controlled disposal area.
A new application of these wastes is the manufacture of sulphur polymer concrete (SPC) a civil engineering material. The advantages of SPC over Portland cement concrete are: quick hardening and reaching the required characteristics in only 24 h; high strength and fatigue resistance; very low water permeability; exceptional resistance to acid and salt agents, which allows its use in extremely aggressive environments; it can be produced and installed throughout the year, regardless of weather conditions, and it can be recycled (Mohamed and El Gamal 2010). This material also allows the utilization of large amounts of sulphur from worldwide oil refineries and metallurgical industries. Also SPC have recently emerged as stabilizing agent for various wastes (López et al. 2009).
So the main objective of the study was the optimization of phosphogypsum (PG) and non dissolved ilmenite mud (MD) on the mixture of SPC, and the physico-chemical and mechanical characterization of sulfur polymer cements manufactured with these waste.

2. Experimental

2.1 Materials

The raw materials used for this study were a granular elemental sulphur (S) (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 sulphur containing polymer (STX^{TM} supplied by Starcrete^{TM} Technologies Inc. Québec, Canada) was used as thermoplastic material (STARTcrete^{TM}, 2000). The STX^{TM} avoid the transformation of the Sβ to orthorhombic Sα, which is stable form at ambient temperature. The S*α* form is denser than S*β* and high stress is induced in the material by solid sulphur shrinkage, disappearing the plastic properties of sulphur (McBee and Sullivan, 1979, López et al., 2011).
The hazardous wastes samples used were phosphogypsum (PG) supplied by the Fertiberia factory of Huelva in 2009. And non-dissolved ilmenite mud (MD) supplied by Tioxide factory of Huelva in 2011. Both wastes were dried at 50 ºC for 48 h.

2.2 Sample preparation

The mixture of typical SPC's was listed in Table 1. The ratio of gravel/sand and sulfur/modified sulfur (STX^{TM}) were maintained constant at 0.5 and 10 for all samples (López, 2009). It should be noted that the percentage of modified sulphur plays an important role in the workability and mechanical strength of SPC (MCBee and Sullivan, 1979). PG and MD have been added to the mixtures at dosages between 10 and 30 wt %.
A total of 7 SPC samples were prepared, a reference one (SPC) and three sulphur polymer cements samples containing phosphogypsum (SPC-PG) and three mud (SPC-MD). Each of the samples were denominated as SPC-X Y-Z where "X" is the waste incorporated in the SPC (phosphogypsum or mud), "Y" is the percentage (wt.%) of elemental sulfur and "Z" is the percentage (wt.%) of the waste in the mixtures. The SPC samples were prepared according as (López, 2011).

2.3 Sample characterization

The major elements are measured for XRF with a Bruker S4 Pioneer. The crystalline phases in wastes were identified by X-ray with a Bruker D8 Discover diffractometer with Kα Cu. The measurement of trace elements was performed by ICP-OES using a Jobin Yvon ULTIMA 2. Granulometry analyses are achieved by using the Mastersize 2000 APA 2000 model.
The mechanical properties of the SPCs samples were measured according to the standard UNE 196-1:2005 (UNE-EN 196-1). Compressive strength was measured for samples cured at ambient temperature for 1 day of age. It is not necessary a longer period time, because it is clear that the 80 % of its ultimate SPC's compressive strength was developed in 1 day (Lopez, 2009; Tayibi et al. 2011b). In addition, the test for Ordinary Portland Cement (OPC) has been carried out.
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 Eq. 1-3. The total pore volume was determined by the Eq. 4:

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

$$P_c(\%) = \left[\left(1-\frac{\rho_s}{\rho_r}\right)\right] x\,100 \quad (2)$$

$$P_{Hg}(\%) = [P_T - P_c] \quad (3)$$

$$V_p = \left(\frac{1}{\rho_b} \quad \frac{1}{\rho_r}\right) \quad (4)$$

The coefficient of water absorption by capillarity (WAC) is a measure of water permeability. The WAC of the test materials was determined gravimetrically UNE-EN 480-5:2006 (UNE-EN 480-5).

Table 1. Composition of SPC-PG and SPC-MD (expressed as wt. %). Compressive and flexural strength (Cs, Fs) for 1day of age and ratio S/waste

Samples	S	Gravel	Sand	PG	MD	STX^{TM}	S/wast.	Cs (MPa)	Fs (MPa)	S/wastes
SPC 21*	21.00	23.10	46.14	0.00	0.00	2.10	------	57.70 ± 1.98	7.07 ± 0.66	-----
SPC-PG 17-10	17.00	23.77	47.53	10.00	0.00	1.70	1.70	55.41±1.37	9.36±0.24	1.70
SPC-PG 19-20	19.00	19.70	39.40	20.00	0.00	1.90	0.95	62.11±0.86	11.20±0.14	0.95
SPC-PG 21-30	21.00	15.63	31.27	30.00	0.00	2.10	0.70	56.76±5.20	10.72±0.60	0.70
SPC-MD 17-10	17.00	23.77	47.53	0.00	10.00	1.70	1.70	58.45 ± 3.82	9.83 ± 1.82	1.70
SPC-MD 21-20	21.00	18.97	37.93	0.00	20.00	2.10	1.05	64.38 ± 1.62	13.25 ± 0.77	1.05
SPC-MD 21-30	21.00	15.63	31.27	0.00	30.00	2.10	0.70	36.77 ± 2.58	9.40 ± 0.52	0.70

*10 % calcium carbonate; Ratio Gravel/Sand= 0.50; ratio Sulphur/STX^{TM}= 10.00

3. Result and discussion

3.1 Characterization of raw material

The main components in PG are CaO and S (expressed as SO_3), as expected their percentage it is close to 90 % of total. In PG was also found P_2O_5 in a 0.96%, which remains in PG later the washing in the industrial process, Table 2. The mud samples present high concentration of TiO_2 (53%). It contains appreciable amounts of iron and silicon oxides, 12.5% and 11.88 %, similar to the observed for other author. The concentration of S (expressed as SO_3) is approximately 7.8 %, which is unsurprising if we consider that the mineral digestion where the mud is generated is carried out with concentrated sulphuric acid (Gázquez, 2009).

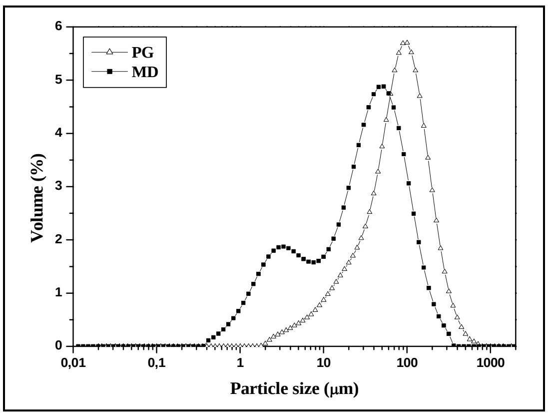

Figure 1. The particle size distribution of wastes samples (PG and MD)

Figure 1a shows the percentage of particles of PG and MD samples, by volume. The d (0.5) value of the particle measured to PG and MD were equal or less than the 53 µm and 30 µm. So the particle size of the

MD is slightly fine than the PG sample. This higher fineness in the mud samples diminishes the workability of the SPC-MD. In the samples with a content of 20 % of MD is necessary an increase in the content of S (21 %) and modified sulphur (2.10 %), with a ratio S/mud of 1.05 higher than in the SPC-PG19-20 with a ratio S/PG of 0.95, see Table 1. The same behaviour is observed in SCP-MD 21-30 a worse workability than SPC-PG 21-30. In PG samples two crystalline phases can be clearly observed by XRD, gypsum and bassanite. It is also observed a less intensity diffraction lines in 26.64 2θ corresponding an impurity of quartz (López et al., 2011).

In the diffractogram obtained for MD, several species are observed: ilmenite, rutile, such as zircon, quartz and Fe and Ti oxides ($Fe_3Ti_3O_{10}$) (Gázquez, 2011). The presence of rutile and the detection of the zircon and quartz cannot be considered as surprising, since all of these species are insoluble in sulphuric acid.

Table 2. Concentration (%) of major elements in raw material

Component	PG	MUD	Gravel	Sand
LOI	2.40	11.19	7.86	8.90
SiO_2	2.43	11.88	29.12	79.89
Al_2O_3	0.40	1.44	1.27	10.75
CaO	40.30	0.73	57.83	0.42
Fe_2O_3	0.23	12.49	0.80	0.74
TiO_2	0.04	52.92	0.13	0.11
SO_3	52.41	7.79	0.27	-----
P_2O_5	0.95	0.02	-----	-----

3.2 Characterization of wastes SPC cements

The compressive and flexural strength in the SPCs cements is shown in Table 1. The Cs of the SPCs with wastes have a value between 55 to 62 MPa and 36 to 64 MPa, it is function of the content of PG or MD in the mixed samples.

In this sense, some authors have reported similar compressive strength. For example Lopez et al. (2009 a) present values of 54 and 58 MPa for metacinnabar SPC, with a rate sulphur/HgS of 0.4 and 2.6 and Mohamed et al. (2007) obtained compressive strength of 54 MPa for SPC with fly ash, with a relation of sulphur/fly ash of 0.9.

These results were compared with Cs and Fs of a Portland Cement (PC) 52.5 N/mm^2. The results obtained to OPC were Fs of 10.1 ± 1.2 MPa and Cs of 61.3 ± 1.0 MPa for 28 days of age. The strength of OPC are similar or slightly lower than the values obtained for the SPC with a percentage between 20 and 30% of PG and 10 and 20 % of MD in one day of age, see Table 1.

Table 1 shows the desired optimum amount of sulphur to wastes (PG and MD) ratios according to the mechanical strength of the SPC samples. The obtained strength tends to increase as the sulphur/wastes ratios increases up between 0.95 and 1.05, when all the particles are coated with a thin layer of sulphur, which acts as a good binder for aggregate particles and finally leads to increase strength. However with a large addition of sulphur, the compressive strength decreases, because a further increment of sulphur increases the thickness of sulphur layers around the aggregates particles and leads to increased brittleness of the composite materials formed.

These results indicate that the polymeric matrix can incorporate a high content of PG and MD (20%) with a relation sulphur/waste between 0.95 and 1.05 without a significant modification of the mechanical properties.

A decrease in total pore volume and in the porosities it is observed in the SPC samples manufactured with the wastes, PG and MD, Table 3. These results showed that the incorporation of PG and MD to the SPC do not change the physical properties of SPC when the PG or MD is added in the 10-30% weight range, if not even diminish the total porosity of the samples.

Similar values of porosity have been obtained by López et al. (2009a, b) 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 amount of mercury increases. The WAC values, Table 4, are very small; they are in agreement with the porosity values for the polymeric cements (Table 3).

After 28 days, the SPC-PG 21-30 showed a WAC coefficient over 33% higher than that of the SPC-21, however, the SPC-MD 21-20 showed a WAC coefficient lesser than the reference sample SPC 21. All WAC values to SPC-PG and SPC-MD samples, are smaller than those for concrete made from Portland cement, the WACs coefficients of 5.0 kg m^{-2}after 28 days of immersion in water are measured for an ordinary Portland cement (Medeiros and Helene, 2009). The use of a sulphur/modified sulphur mix reduces the WAC coefficient, producing a very impermeable concrete.

On the SPC samples were studied the leaching of radionuclides at different pH (2-10). The result showed that the leaching values of radionuclides are always under international recommendation, thus, contamination of waters from these and other radionuclides tested can be considered negligible.

Table 3. Total pore volume (V_p) and total (P_T), close (P_C) and open (P_{He}) porosity

Samples	SPC 21	SPC-PG 17-10	SPC-PG 19-20	SPC-PG 21-30	SPC-MD 17-10	SPC-MD 21-20	SPC-MD 21-30
V_p (x10^{-2}) (cm^3 g^{-1})	5.71	2.51	2.92	1.19	2.07	1.10	1.37
P_T (%)	12.45	5.95	6.80	2.85	5.06	2.73	3.45
P_C (%)	2.01	2.38	2.00	1.63	4.67	2.73	2.68
P_{He} (%)	10.44	3.57	4.80	1.22	0.39	0.00	0.77

Table 4. Water absorption by capillarity as a function of time for cement with and without mud

Mixture	Water absorption (kg m^{-2})			
	3 h	72 h	7 d	28 d
SPC 21	0.07	0.20	0.30	0.90
SPC-PG 21-30	0.10	0.16	0.20	1.20
SPC-MD 21-20	0.10	0.40	0.50	0.60

4. Conclusions

The results obtained confirm that the valorisation of phosphogypsum (PG) and non-dissolved ilmenite mud (MD) it is possible with a solidified material with an optimal mixture ratio of sulfur/phosphogypsum = 1:0.9 and sulphur/mud = 1:1 and a waste dosage between 10-30 wt%. These SPC samples resulting in highest strength (55 to 62 MPa to SPC-PG and 36 to 64 MPa to SPC-MD) and low total porosity between 2.8 and 6.8 % in the PG-SPC and 2.7 to 5.1 in PG-MD samples. At all the study time the values of water absorption capillarity to SPC-PG and SPC-MD samples, are smaller than those for concrete made from Portland cement.

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