Valorisation of waste ilmenite mud in the manufacture of sulphur polymer cement

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ABSTRACT

This paper reports the preparation of sulphur polymer cements (SPCs) incorporating waste ilmenite mud for use in concrete construction works. The ilmenite mud raw material and the mud-containing SPCs (IMC-SPCs) were characterised physico-chemically and radiologically. The optimal IMC-SPC mixture had a sulphur/mud ratio (w/w) of 1.05 (mud dose 20 wt %); this cement showed the greatest compressive strength (64 MPa) and the lowest water absorption coefficient (0.4 $g.cm^{-2}$ at 28 days). Since ilmenite mud is enriched in natural radionuclides, such as radium isotopes ($2.0\cdot10^{3}$ Bq kg^{-1228}Ra and $5.0\cdot10^{2}$ Bq kg^{-1226}Ra), the IMC-SPCs were subjected to leaching experiments, which showed their environmental impact to be negligible. The activity concentration indices for the different radionuclides in the IMC-SPCs

containing 10% and 20% ilmenite mud met the demands of international standards for materials used in the construction of non-residential buildings.

Key words: naturally occurring radioactive materials (NORM), titanium dioxide industry, ilmenite mud, sulphur polymer cements.

1. INTRODUCTION

The immobilisation/stabilisation of pollutants and the valorisation of hazardous industrial wastes is an area of great environmental and economic interest (Chen et al., 2010; Cruz-Yusta et al., 2011; Puertas et al., 2008;Yan et al., 2011). This paper describes the stabilisation and valorisation of waste ilmenite mud, generated in the titanium dioxide industry, as a component of sulphur polymer cement (SPC) that could be used in concrete construction works.

TiO_2production begins with the mixing of ilmenite and highly concentrated sulphuric acid (80-95%). The liquor generated is passed to a clarification tank where the un-attacked solid - ilmenite mud - is allowed to settle. This mud is finally separated from the liquor by decantation and filtration (Gázquez et al., 2011). It is then neutralised and usually stored in a safe area.

Sulphur polymer cements have advantages over regular Portland cement in that they harden in under 24 h, are of high compressive strength, show resistance to fatigue, are little permeable to water, show exceptional resistance to acid and salt (allowing their use in aggressive environments such as sea water, and under all weather conditions),and are recyclable (ACI Committee 548, 1993; Amo and El Gamal, 2009). In addition, SPC manufacture could make use of large amounts of sulphur waste, e.g., from oil refineries and the metallurgical industry. SPCs can also be used as stabilising agents for other kinds of waste (López et al., 2009; López et al., 2011; Mohamed and Gamal, 2007; Sandrolini et al., 2006), including – potentially - ilmenite mud. Unfortunately, this type of mud contains relatively large amounts of natural radionuclides (Gázquez et al., 2011); its immobilisation in SPCs used in the construction of occupied buildings might therefore put people at risk. International recommendations exist (Radiation Protection 112, 1999) that propose reference values for natural radionuclide concentrations in building materials; Eq. (1) shows how the exposure risk index (I) is calculated:

$$I = \frac{C_{226_{Ra}}}{300\ Bq/kg} + \frac{C_{232_{Th}}}{200\ Bq/kg} + \frac{C_{40_K}}{3000\ Bq/kg} \quad \text{Eq. (1)}$$

where C(^{226}Ra), C(^{228}Ra) and C(^{40}K) are the respective activity concentrations for ^{226}Ra, ^{228}Ra and ^{40}K in the building material considered (expressed in Bq kg^{-1}). It is recommended that building material-induced indoor gamma doses do not exceed 1 mSv per year.

In addition, ilmenite mud also contains a number of metals. If these were to leach out of ilmenite mud-containing SPCs (IMC-SPCs), they too could cause environmental and public health problems.

The aims of the present work were: (1) to study the stabilisation of ilmenite mud as an additive in SPCs, allowing its valorisation as a component of building materials, and (2) to characterise the mechanical properties of IMC-SPCs, their long-term stability, and their potential environmental impact.

2. MATERIALS AND METHODS

2.1 Materials

The raw materials used to make the SPCs examined in this work were granular elemental sulphur (99.4 wt%, size <60 µm, type Rubber Sul 10) (Repsol-YPF, Madrid, Spain), gravel (<6.3 mm) and a siliceous sand (<4 mm). A modified sulphur-containing polymer, STX™ (StarcreteTM Technologies Inc., Québec, Canada), was used as a thermoplastic material in all the SPCs made. STX™ prevents crystalline changes inside SPCs when these are exposed to changing temperatures over time(STARTcrete™). The ilmenite mud sample was supplied by Huntsman-Tioxide (Huelva, Spain). It was dried at 50ºC for 48 h before use.

2.2 Preparation of SPC

Table 1 shows the SPCs produced. These included three IMC-SPCs made with different doses of ilmenite mud (10, 20 and 30% w/w [SPC17-10, SPC21-20 and SPC21-30 respectively]), and a control SPC (SPC21-0) with no ilmenite mud but containing 99.5% pure, inert calcium carbonate (7.69% w/w) (Panreac(R), Barcelona, Spain). (Note: the SPC17-10 was prepared with 17% instead of 21% sulphur to optimise the workability of the product). All these SPCs were prepared using a sulphur/STX™ ratio of 10 and a gravel/sand ratio of 0.5. Previous studies (Lopez et al., 2009; McBee, 1979;Sandrolini et al., 2006) have shown these ratios to produce final mixtures of optimum viscosity and workability. A sample of Ordinary Portland Cement (OPC) was also produced (sand/cement ratio 3:1).

Table 1
Composition of IMC-SPCs (expressed as wt%) (gravel/sand ratio 0.50; sulphur/STX™ ratio 10.00).

Code	Elemental sulphur (%)	Gravel (%)	Sand (%)	Mud (%)	STX™ (%)	Sulphur/ mud ratio
SPC21-0[a]	21	23.07	46.14	0	2.10	–
SPC17-10	17	23.77	47.53	10	1.70	1.70
SPC21-20	21	18.97	37.93	20	2.10	1.05
SPC21-30	21	15.63	31.27	30	2.10	0.70

[a] 7.69 wt% calcium carbonate.

To prepare the SPCs, the aggregates (gravel, sand and mud) were heated in an oven to 135–140ºC for 4 h. The sulphur was liquefied in a mixing bowl within the same temperature range for 10 min. These materials were then mixed into a homogeneous viscous paste. At this point, STX^{TM} was added, stirring for 4–5 min at 140–145ºC. Temperature control is important in this process since temperatures of >145ºC can induce unwanted reactions between the STX^{TM} and the sulphur, leading to a poorly workable, highly viscous final material. Steel moulds (40×40×160 mm) were preheated to approximately 120ºC and the forming SPCs poured into them. A vibration table set at 3000 rpm for 30 s was employed to compact the cements in the moulds before storing them at room temperature for 24 h. The hardened SPCs casts were then de-moulded.

2.3 Characterisation of the raw materials used and SPCs produced

Major elements were determined in the ilmenite mud, sand and gravel by X-ray fluorescence (XRF) using a Bruker S4 Pioneer system (4 kW, Rh front window and anode, five analysing crystals [LIF200, Ge, PET, OVO55 and OVOC] and two X-ray detectors). This technique requires the samples under analysis to be as homogeneous as possible. Thus 1 g samples of each dry SPC or original ilmenite mud were ground using a pestle and mortar. The ground samples were then mixed with 10 g of lithium tetraborate and 5 drops of 20% lithium iodide to form a homogenous glass ready for examination.

Granulometric analyses of the ilmenite mud, gravel and sand were performed using a Mastersize 2000 APA granulometer (Malvern Instruments Ltd.). For this, some 20-30 g of each of these raw materials were placed in deionised water for 24 h. They were then placed in a flask and mixed using a magnetic stirrer at a constant speed to ensure the homogeneous distribution of the particles. Aliquots were then collected for granulometric analysis.

The compressive (Cs) and flexural (Fs) strengths of the SPCs were measured according to standard UNE 196-1:2005, using an Autotest 200-10-W universal press (Ibertest). Only one day of curing was necessary before performing this test with the SPC casts since 80% of the final values reached are achieved within this time (López et al., 2009; López et al., 2011; Sandrolini et al., 2006). Values for the OPC casts were measured at 28 days of curing. All tests were performed in sextuplicate.

The coefficient of water absorption by capillarity (WAC - a measure of permeability) was determined gravimetrically according to standard UNE-EN480-5 (2006). Casts of two of the IMC-SPCs made with ilmenite mud (SPC17-10 and SPC21-20), and the control SPC (SPC21-0) (Table 1), were dried at 50°C in an oven until a constant mass was reached. They were then placed on a grating in a dish of water (at room temperature), the liquid being allowed to wet only their lower surfaces. The lower parts of the sides adjoining the inflow face were sealed with a polyethylene sheet to prevent any water being absorbed into their surface pores. All experiments were performed in triplicate. The WAC values were then determined using Eq. (2):

$$WAC = \frac{\Delta M}{A} = \frac{M_j - M_0}{16} \qquad \text{Eq. (2)}$$

where M_j is the sample mass after 28 days, M_o the initial mass, and '16' the wetted surface area of the sample (4x4 cm).

The coefficients of absorption (A_C) with respect to the pH were determined by placing the different casts in deionised water for 24 h. They were then weighed, immersed for

42 days in buffers at pH 2, 4, 6, 8 or 10, and reweighed. The A_C value for each cement was then determined using Eq. (3), (Félix et al., 2011):

$$A_C(\%) = \frac{P_{3i} - P_{1i}}{P_{1i}} \cdot 100 \qquad \text{Eq. (3)}$$

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

2.4 Radioactive characterisationof the starting ilmenite mud, SPCs and SPC leachates

Samples of the SPCs and mud were ground with a pestle and mortar. The activity concentration of ^{226}Ra was then determined at 352 keV (via the emission of ^{214}Pb), that of ^{228}Radetermined at 911 keV (via the emission of ^{228}Ac), and that of ^{228}Th at 583 keV (via the emission of ^{208}Tl) (always taking into account the branching ratios in the decay of these nuclides), using a gamma spectrometer (38% relative efficiency, full width at half maximum FWHM 0.95 keV at the 122 keV line of ^{57}Co and 1.9 keV at the 1333 keV line of ^{60}Co (Pérez-Moreno et al., 2002)).

^{210}Po and the Th and U isotopes were dissolved out of the SPCs and isolated using a well-established sequential radiochemical method (Oliveira and Carvalho, 2006). The poor solubility of the ilmenite mud required the use of a total dissolution method based on $KHSO_4$ fusion previously validated by our group (Mantero et al., 2010). After isolation, the U and Th isotopes were electrodeposited independently onto stainless steel discs. The ^{210}Po was obtained by self-deposition on silver discs. The activity concentration of all three nuclides was then measured using an EG&G Ortec alpha-particle spectrometer system.

The ^{210}Po and the Th and U isotopes in the leachates from the SPCs (see below) were electrodeposited in the same way before analysis. The isotopes of Ra were measured directly.

2.5 Leaching test

The mobilities of the radionuclides and metals in the manufactured SPCs were determined by leaching tests performed at different pHs. The procedures followed were the same as those described for the determination of Ac. At 42 days, the radionuclide concentrations of the buffer solutions were determined as described above. The radionuclide concentrations of the original buffers (i.e., before being used in the leaching test) were also determined.

The leaching coefficient (L_c) for ^{238}U and ^{210}Po at each pH was determined according to Eq. (4), (Félix et al.,2011):

$$L_C(\%) = \frac{A_L(Bq\ L^{-1})}{A_S(Bq\ L^{-1})} \cdot \frac{V_t(L)}{P_{1i}(g)} \cdot 100 \qquad \text{Eq. (4)}$$

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 cement sample (expressed as Bq g^{-1}), and P_{1i} the mass of the sample after 24 h of immersion in water (expressed in g).

The concentrations of a number of metals in the leachates were determined by inductively coupled plasma optical emission spectrometry using an Jobin Yvon ULTIMA 2 apparatus. The system was calibrated using appropriate standards. Leachate samples were diluted to 2% in a nitric acid solution for introduction into the apparatus.

3. RESULTS AND DISCUSSION

3.1 Characterisation of raw materials

Table 2 shows the concentrations (% dry weight) of the major elements in the raw materials and ilmenite mud used to make the SPCs. The mud had a TiO_2 content of 53 wt%, and contained appreciable amounts of iron oxide (12.5 wt%) and silicon oxide (11.9 wt%). These figures are similar to those reported by other authors (Gázquez et al., 2011). It also contained non-negligible concentrations of Al, Mg and Ca. Its S concentration (expressed as SO_3) was approximately 7.8 wt%; this is not surprising given that the digestion process in which the mud is generated involves the use of concentrated sulphuric acid (Gázquez et al., 2009a).

Table 2
Concentration (% dry weight) of major elements in the raw materials used to make the cements, and LOI values.

Samples	Mud (%)	Gravel (%)	Sand (%)
Loss on ignition (L.O.I.)	11.2	7.86	8.90
SiO_2	11.9	29.12	79.89
Al_2O_3	1.44	1.27	10.75
CaO	0.73	57.83	0.42
Fe_2O_3	12.5	0.80	0.74
MgO	0.94	0.63	0.26
TiO_2	52.9	0.13	0.11
SO_3	7.79	0.27	–
Na_2O	0.16	–	1.78
K_2O	0.16	0.25	5.30
P_2O_5	0.02	–	–

Figure 1a shows the distribution of raw gravel and sand particle size against the Spanish Standard for structural concretes (Real Decreto 2661/1998); both materials met the requirements for use. Figure 1b shows the percentage (by volume) of particles in the ilmenite mud with a diameter between 1 and 2000 µm. The median $d_{0.5}$ of the particle distribution was <30 µm and the $d_{0.9}$ value <107 µm.

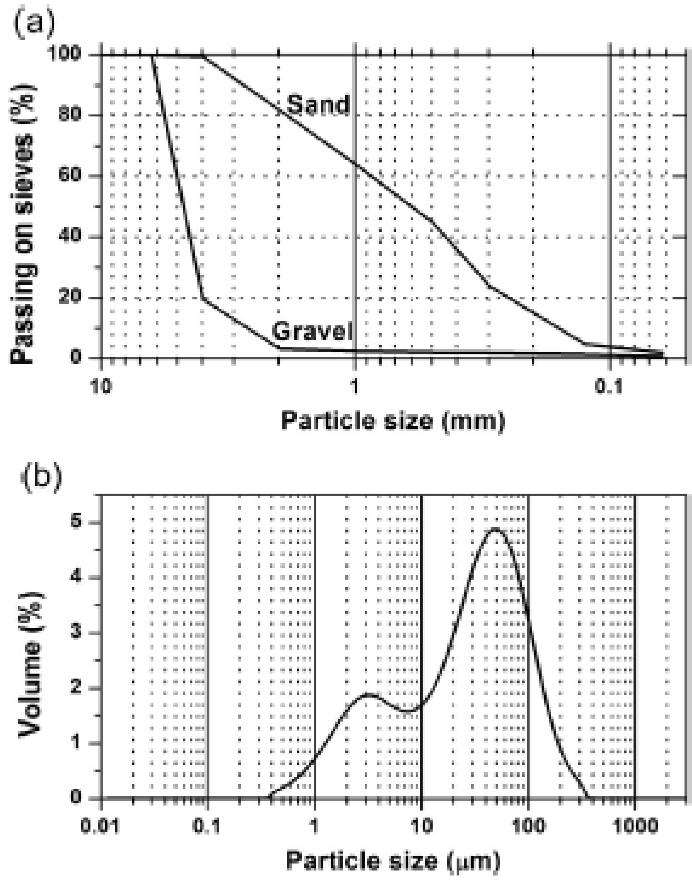

Fig. 1. Particle size distribution for: a) sand and gravel, and b) ilmenite mud.

Figure 2 shows the mineralogical composition of the ilmenite mud as determined by XRD. The minerals detected included ilmenite, rutile, zircon ($ZrSiO_4$), quartz (SiO_2) and $Fe_3Ti_3O_{10}$. The presence of rutile, zircon and quartz is not surprising since all are insoluble in sulphuric acid (McNulty, 2007).

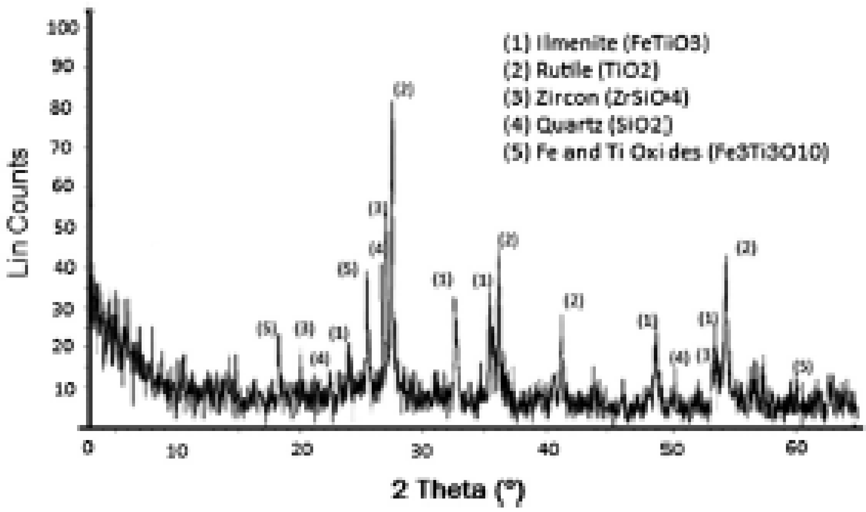

Fig. 2. XRD pattern of the ilmenite mud.

Figure 3 shows the diffractograms for sulphur and STX^{TM}. The diffraction lines appearing at 22.8º and 27.8° (2θ) for the modified sulphur STX^{TM} correspond to the S_{β} crystalline phase. These lines are better observed in the magnifications provided in the upper right corner of the figure.

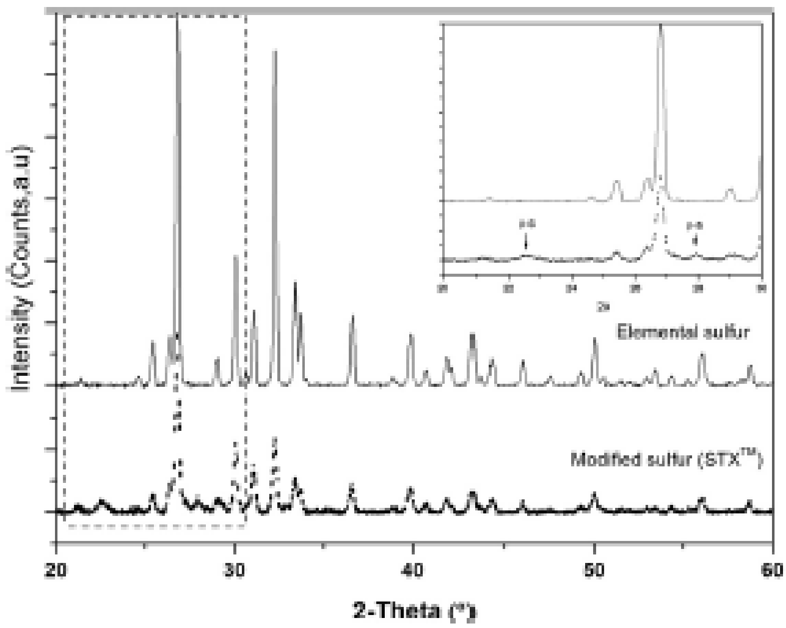

Fig. 3. XRD patterns of sulfur and sulfur modified (STX^{TM}).

3.2 Compressive and flexural strengths of the SPCs, and their WAC and Ac values

Table 3 shows the Fs and Cs values recorded for the different SPCs. SPC21-20 returned the highest Cs (64 MPa). López et al. (2009), reported values of 54 and 58 MPa for metacinnabar-containing SPCs with sulphur/HgS ratios (w/w) of 0.4 and 2.6 respectively, and of 62 MPa for a phosphogypsum-containing SPC with a sulphur/phosphogypsum ratio of 0.9 (López et al., 2011). Mohamed and Gamal (2007) reported a Cs of 54 MPa for an SPC manufactured with fly ash and with a sulphur/fly ash ratio (w/w) of 0.9. Sandrolini et al. (2006) reported a Cs of 65-73 MPa for an SPC made with an aggregate recycled from the ceramics industry. Ordinary Portland cement (OPC) contains clinker (97%) and natural gypsum (3%), and has a Cs of >52.5 MPa after 28 days of curing, as determined according to standard UNE-EN 196-1 (2005). In the present work, the OPC had an Fs of 10.1±1.2 MPa after 28 days of curing, and a Cs of 61.3±1.0 MPa, values similar to or slightly lower than those returned by SPC17-10 and SPC21-20 after just one day of curing (Table 3). The Cs increased as the sulphur/mud ratio increased up to 1.05 (that used in the manufacture of SPC21-20), at which point all the particles would have been coated with a thin layer of sulphur. This would act as a good binder for the aggregate particles, increasing the final Cs. However, the addition of more sulphur (i.e., in the SPC21-30 mixture) would have produced a thick layer of sulphur around the aggregates, increasing the brittleness of the final composite. Given the poor Cs value recorded for SPC21-30, this cement was left out of all further analyses.

Table 3
Flexural and compressive strengths (MPa) of the SPCs after 24 h of curing and OPC (Ordinary Portland Cement) after 28 days.

Code	Flexural strength (MPa)	Compressive strength (MPa)
SPC21-0	7.1 ± 0.6	57.7 ± 2.0
SPC17-10	9.8 ± 1.8	58.4 ± 3.8
SPC21-20	13.2 ± 0.8	64.4 ± 1.6
SPC21-30	9.4 ± 0.5	36.8 ± 2.6
OPC	10.1 ± 1.2	61.3 ± 1.0

After 28 days, SPC21-20 returned a WAC value of 0.6 kg m^{-2}, slightly lower than the 0.9 kg m^{-2} of the SPC21-0. However, both values are smaller than those reported for Portland cements. For example, Khatib and Clay (2004) report a WAC of 5.0 kg m^{-2} for OPC after 28 days of immersion in water, while Medeiros and Helene (2009) report a value of 6.2 kg m^{-2} for Brazilian Portland cement (CPII E-02 or slag-modified Portland cement) after the same immersion time. SPC21-20 would therefore appear to be a very impermeable SPC.

Table 5 shows the A_c values for the different SPCs. The SPC21-0 control had a higher A_c than SPC17-10 and SPC21-20 over the full pH range tested (1.63% at pH 2 to 0.75% at pH 10, compared to a practically constant 0.4-0.5% for both of these IMC-SPCs).

Table 5
Water absorption coefficients, ^{238}U and ^{210}Po concentrations, and leaching coefficients with respect to pH.

Code	pH	A_c (wt %)	^{238}U (Bq L^{-1})	^{210}Po (Bq L^{-1})	^{238}U L_c (%)	^{210}Po L_c (%)
Reference	2	1.63	0.08 ± 0.003	<0.01	0.27	<0.01
SPC21-0	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
SPC17-10	2	0.37	0.124 ± 0.008	0.036 ± 0.002	0.18	0.05
	4	0.33	0.109 ± 0.009	0.029 ± 0.003	0.16	0.04
	6	0.40	0.137 ± 0.007	0.026 ± 0.002	0.20	0.04
	8	0.45	0.011 ± 0.002	0.009 ± 0.001	0.02	0.01
	10	0.48	0.002 ± 0.001	0.013 ± 0.002	<0.01	0.02
SPC21-20	2	0.37	0.463 ± 0.025	0.158 ± 0.016	0.26	0.16
	4	0.36	0.363 ± 0.078	0.132 ± 0.008	0.30	0.13
	6	0.34	0.340 ± 0.020	0.113 ± 0.006	0.20	0.11
	8	0.38	0.111 ± 0.008	0.093 ± 0.008	0.18	0.10
	10	0.46	0.009 ± 0.004	0.011 ± 0.002	0.05	0.01

3.3 Radiological characterisations

3.3.1 *Activity concentrations and activity concentration indices of the ilmenite mud and SPCs*

Table 4 shows the results of the radioactive characterisation of the ilmenite mud and SPCs. The original mud had a total radionuclide concentration (2.5–3.0 Bq g^{-1}) that surpassed the 1 Bq g^{-1} EU safety threshold for naturally occurring radioactive material (NORM) wastes (IAEA, 2004). The radionuclides with the highest activity concentrations were ^{226}Ra and ^{228}Ra at around 520 and 1900 Bq kg^{-1} respectively (Gázquez et al., 2009b; Gázquez et al., 2011). These concentrations are significantly higher than the average worldwide values for soils (25 Bq·kg^{-1} of ^{238}U and ^{232}Th in secular equilibrium with their daughters) (UNSCEAR, 1993). In the IMC-SPCs, the activity concentration of these radionuclides increased with increasing mud content, as did those of ^{210}Pb, ^{228}Th, and ^{238}U. The activity concentration of ^{40}K decreased as the mud content increased.

Table 4
Activity concentrations (Bq kg^{-1}) of radionuclides in the IMC-SPCs and the original ilmenite mud. The activity concentration index "*I*" is also shown.

Code	SPC21-0	SPC17-10	SPC21-20	SPC21-30	MUD
MUD (%)	0	10	20	30	100
^{210}Pb	8.0 ± 0.6	28 ± 4	40 ± 4	76 ± 7	247 ± 11
^{238}U	12 ± 2	25 ± 4	61 ± 5	84 ± 7	184 ± 12
^{226}Ra	7.4 ± 0.5	51 ± 3	123 ± 7	194 ± 11	521 ± 30
^{228}Th	8.8 ± 0.8	50 ± 2	100 ± 6	168 ± 11	510 ± 30
^{228}Ra	8.2 ± 0.8	212 ± 13	426 ± 26	674 ± 39	1919 ± 112
^{40}K	580 ± 30	512 ± 31	493 ± 32	413 ± 24	334 ± 21
INDEX "*I*"	0.26	1.4	2.7	4.2	11.4

The activity concentration index (*I*) of all the SPCs was higher than the EU reference value for occupied buildings (Radiation Protection, 112, 1999). This index should not exceed 1 for any material used in bulk quantities, e.g., concrete. Nevertheless, the present IMC-SPCs could have other civil construction applications, e.g., in marine platforms or bridges, since their radiological impact on the environment is negligible, as shown below.

3.3.2 *Environmental mobility of radionuclides in leaching tests*

Neither ^{226}Ra, ^{234}Th, ^{228}Ra, ^{40}K nor ^{210}Pb were detected in the leachates of any SPC, leading to inappreciable L_c values. ^{238}U and ^{210}Po were detected among the alpha particle emitters. Th isotope levels were below the detection limit in most of the samples tested (0.5-1 mBq). This is explained in that Th tends to bind strongly to particulate matter.

The highest activity concentration of ^{238}U in the SPC21-0 leachate was 0.14 Bq L^{-1} at pH 4, and 0.01 Bq L^{-1} at pH 8, similar to the values recorded for inland water bodies (typical range 0.005–0.5 Bq L^{-1}) (Más et al., 2006). The SPC17-10 leachate had a ^{238}U activity concentration of around 0.12 Bq L^{-1} in the acidic buffers (pH 2-6), falling to 0.01 Bq L^{-1} at pH 8, and 0.002 Bq L^{-1} at pH 10. The SPC21-20 leachate returned similar results. The contamination of water by U isotopes by the present IMC-SPCs would therefore be negligible.

Table 5 shows the activity concentrations recorded for ^{210}Po to be one third those recorded for ^{238}U (Más et al., 2006) at pH 2, 4 and 6 in all the SPC leachates examined. The ^{210}Po activity concentrations for SPC21-0 were 0.039 Bq L^{-1} at pH 4 and 0.017 Bq L^{-1} at pH 6, values higher than those obtained at pH 8 and pH 10. The SPC17-10 leachate returned ^{210}Po activity concentrations over the pH 2-6 range similar to those of SPC21-0, while at pH 8 and pH 10 the values were higher, although of the same order of magnitude as reported for continental waters (Más et al., 2006). The ^{210}Po in the SPC21-20 leachate clearly decreased with pH but levels were below the Spanish threshold for this radionuclide in drinking water.

Table 6 shows that Pb, Cd, As and other elements in the leachates were below their detection limits. No significant differences were seen between SPC17-10 and SPC21-20, indicating these pollutants to be very well bound to the cement matrix. Mg, Al, Ti, Mn and Fe were more mobile at low pHs (especially pH2). The K concentrations of the leachates were highest at pH 10.

Table 6
Composition of the leachates at different pHs.

Code	SPC17-10					SPC21-20				
pH	2	4	6	8	10	2	4	6	8	10
Na ($g L^{-1}$)	0.40	0.40	0.80	0.30	0.20	0.30	0.40	0.50	0.20	0.20
Fe ($g L^{-1}$)	0.14	0.13	0.12	0.03	0.01	0.10	0.10	0.10	0.10	0.04
K ($g L^{-1}$)	0.01	0.06	0.01	0.01	0.20	<0.01	<0.01	<0.01	<0.01	0.10
Mg ($mg L^{-1}$)	90	64	49	57	38	50	49	44	56	47
Al ($mg L^{-1}$)	89	66	49	<5	<5	77	72	60	30	<5
Ca ($mg L^{-1}$)	24	70	30	26	14	<5	<5	25	41	22
Ti ($mg L^{-1}$)	16	14	13	<0.5	<0.5	87	82	41	<0.5	<0.5
Mn ($mg L^{-1}$)	28	25	24	26	<2	39	33	24	39	30
Ni ($mg L^{-1}$)	<2	<2	<2	4	<2	4	4	<2	4	<2
Zn ($mg L^{-1}$)	4	15	<1	2	2	10	5	3	5	2

4. *Economic viability*

In Spain, the Huntsman-Tioxide company produces 64,000 t of TiO_2 every year, and about 30,000 t/year of ilmenite mud waste. According to Decision 2000/532/EC of the European Commission (2000/532/EC), ilmenite mud waste is toxic and dangerous. European Union Landfill legislation (2003/33/EC) establishes that this waste must be safely stored. The costs of such storage differ by country. In Spain, which has great storage capacity but little industrial activity at the present time, these costs are very low at about €100/t. In contrast, in the UK, they are much greater. The cost of making SPC21-20 (including the raw materials and energy required) is some €125/t according to the company Equipos Nucleares S.A. (personal communication), therefore it costs €627 to dispose of 1 t of ilmenite mud waste (SPC21-20 contains 20 wt% ilmenite mud).

SPC21-20 could be used in exactly the same way as the type of concrete used in marine environments. In Spain, such concrete costs about €75/m^3 or €32.6/t. The economic viability of SPC21-20 production, however, ultimately depends on the costs of conventional safe storage of ilmenite mud . The viability of SPC21-20 production is reflected by the equation: *storage cost + sale price – manufacturing costs.* In Spain, production may not be economically viable, but, for example, in the UK, it may well be.

4. CONCLUSIONS

The present results show that ilmenite mud from the TiO_2 industry can be successfully immobilised - and valorised – by including it in the manufacture of SPCs, which themselves allow for the safe disposal of waste sulphur.

SPC17-10 and SPC21-20 showed good mechanical properties. Indeed, no difference was seen between those of SPC21-20 and SPC21-0. The WAC values recorded for the IMC-SPCs were slightly lower than that obtained for the control SPC,and much lower than that reported for Portland cements.

The leaching tests showed the mobility of radionuclides and metals in the IMC-SPCs to be negligible. The leaching coefficients obtained in acidic media were always higher than those obtained in alkaline media, but were always lower than international recommendations.

Although not suitable for the construction of occupied buildings, SPC21-20 in particular could be safely used in concrete construction works, e.g., in the construction of pump foundations, walls for storage areas, underwater joint protections for steel pipes, and sewer systems.

ACKNOWLEDGEMENTS

This work was supported by the Regional Government of Andalusia through the research project "*Characterisation and modelling of the phosphogypsum stacks of Huelva for their environmental management and control*" (grant RNM-6300). Dr. Irene García expresses her gratitude to the Spanish National Research Council (CSIC) for her contract through the JAE Program (JAEDoc-09-00893), co-financed by the European Social Fund.

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