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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 ($2.0 \cdot 10^3$ Bq kg^{-1} ^{228}Ra and $5.0 \cdot 10^2$ Bq kg^{-1} ^{226}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.

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_2 production 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 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, 2011; Mohamed and Gamal, 2007; Sandrolini et al., 2006a, b), 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:

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

where C(^{226}Ra), C(^{232}Th) and C(^{40}K) are the respective activity concentrations for ^{226}Ra, ^{232}Th 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.

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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 (STARcrete™). The ilmenite mud sample was supplied by Huntsman-Tioxide (Huelva, Spain). It was dried at 50 °C 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®, 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 (López et al., 2009; McBee and Sullivan, 1979; Sandrolini et al., 2006a, b) 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).

To prepare the SPCs, the aggregates (gravel, sand and mud) were heated in an oven to 135–140 °C 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™ was added, stirring for 4–5 min at 140–145 °C. Temperature control is important in this process since temperatures of >145 °C can induce unwanted reactions between the STX™ and the sulphur, leading to a poorly workable, highly viscous final material. Steel moulds (40 × 40 × 160 mm) were preheated to approximately 120 °C 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 demoulded.

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.

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, 2011; Sandrolini et al., 2006a,b). 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):

$$\mathrm{WAC} = \frac{\Delta M}{A} = \frac{M_j - M_o}{16} \tag{2}$$

where M_j is the sample mass after 28 days, M_o the initial mass, and '16' the wetted surface area of the sample (4 × 4 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), (López et al., 2011):

$$A_C(\%) = \frac{P_{3i} - P_{1i}}{P_{1i}} \cdot 100 \tag{3}$$

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 characterisation of 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}Ra determined 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