

Recovery of ilmenite mud as an additive in commercial Portland cements

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Abstract

This work is focused on the manufacture of commercial cement using as additive ilmenite mud, a waste generated during TiO₂ pigment production. The cements were produced by adding different proportions of mud (2.5, 5, and 10 wt.%) to ordinary Portland cement (OPC). The ilmenite mud and the ilmenite mud cements (IMCs) were characterised physico-chemically by X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), and X-ray diffraction (XRD). Moreover, the technological properties of the IMCs were evaluated and compared with a reference material (OPC). Since waste from the TiO₂ industry is classified as a NORM (Naturally Occurring Radioactive Material), the concentrations of radionuclides were measured by high-resolution low-background gamma and alpha spectrometry techniques. Finally, the TCLP leaching test (Toxicity Characteristic Leaching Procedure, USEPA), the radiological Index ("I"), and the Ra equivalent concentration were also calculated to evaluate the environmental risks. As a final conclusion, it can be pointed out that the addition of ilmenite mud to OPC plays a beneficial role since it reduces the heat of hydration, the final setting time, the expansion, and the linear retraction compared to standard OPC. The compression strength improves with the addition of up to 5 wt.% mud. Moreover, the environmental impact of IMC2.5 and IMC5 can be considered negligible.

Keywords: Ilmenite mud, titanium dioxide industry, valorisation, Portland cement, NORM, waste.

1. Introduction

Nowadays, the valorisation and recycling of industrial waste in the manufacture of construction materials is an area of great environmental and economic interest (Chen et al. 2010; Cruz-Yusta 2011). The valorisation of wastes as secondary raw materials could mitigate the problems associated with both the depletion of natural resources and the disposal of industrial wastes (Andres 2005; Caligaris 2000; Alsheyaba and Khedaywi 2013). Moreover, the hazardous elements and pollutants contained in the waste are immobilised and stabilised on the matrix material (Puertas 2008; Yan 2011).

There are two main processes for the manufacture of TiO₂ pigment: the sulfate and chloride processes. The sulfate route is used in 70% of European production (Contreras 2017). This method generates a large amount of by-products and waste, as ilmenite mud, the object of study in this research paper. This waste is generated during the digestion of the feedstock (ilmenite ore) with highly concentrated sulphuric acid (80–95%). The liquor generated is passed to a clarification tank, where the unattached solid, called ilmenite mud, is allowed to settle. This mud is finally separated from the liquor by decantation and filtration. It is then stored in a controlled landfill repository because it contains significant concentrations of heavy metals, radionuclides, and residual sulphur, implying a highly acidic pH value. This waste has been classified as "hazardous waste" (European Waste Catalogue and Hazardous Waste List: code 06 01 01*) (Contreras 2017), according to the European legislation [Directive 2008/98/EC on waste (Waste Framework Directive); Commission Regulation (EU) No. 1357/2014 replacing Annex III to Directive 2008/98/EC and Commission Decision 2014/955/EU amending Decision 2000/532/EC on the list of waste pursuant to Directive 2008/98/EC].

The only TiO₂ pigment production factory in Spain is located in the city of Huelva and produces 60 kt of pure TiO₂ pigment and generates about 30 kt of ilmenite mud waste every year without commercial application (Contreras 2017).

Ilmenite mud is characterised by a high content of titanium oxide (TiO₂ ≈ 50% in dry weight) (Gázquez et al. 2011; Contreras et al. 2013, 2014), and for that reason its valorisation in cement has been achieved through its incorporation as additive in the manufacture of Portland cement. Several publications have studied the effect of the addition of titanium dioxide in the production of clinker (Katyál et al. 1999a, b; Knoefel 1979; Potgieter et al. 2002). In all the works mentioned above, the TiO₂ rich materials have been mixed up together in the oven with raw materials to produce clinker. On the other hand, the rheological behavior, thermal and mechanical properties by adding TiO₂ nanoparticles in cement pastes and mortars as additive were also studied (Senff et al 2012; Nazari and Riahi, 2011a, b). In addition, we have found some studies investigating the possibility of adding ilmenite mud directly as an additive, evaluating the hydration process of Portland cement obtained (Bobrowicz J., Chylinski, 2016; U.S. Patent No. 7,824,322 B2, 2010). In these previous studies, the ilmenite mud used come from the chloride process, being their composition similar but not the same that the ilmenite mud collected from sulphate process used in the present manuscript.

In addition, it is essential to study whether the presence of this waste influences the mechanical properties of the cement, checking its environmental impact in relation to the potential problem of leaching metals and radionuclides included in the matrix of the new cement. Moreover, the content of radioactivity in the ilmenite mud must be taken into account because it comes from a NORM (Naturally Occurring Radioactive Material) industry and the content of natural radionuclides is about 100 times higher than in a typical soil according to UNSCEAR (1988).

Taking into account the previous facts, the main objective of this work was to evaluate the addition of ilmenite mud as an additive in the manufacture of commercial cement, carrying out an exhaustive analysis in relation to the technological properties and the environmental implications of the new cements obtained.

2. Materials and Methods

2.1. Materials and sample preparation

The sampling process entailed taking one sample every five days during one month to ensure the homogeneity of the waste collected (six samples). The ilmenite mud was previously dried in an oven at 110 °C for at least 48 h until it reached a constant weight. Several mixtures of cements were manufactured with different concentrations of ilmenite mud as additive (2.5, 5, and 10 wt.%; code samples IMC2.5, IMC5, and IMC10 respectively) in ordinary Portland cement (OPC) type I. This OPC is characterised by a compressive strength category of 52.5 N·mm⁻² and is composed of a mixture of clinker (97 wt.%) and natural gypsum (3 wt.%). Mortar mixtures were prepared using the optimum w/c ration required to obtain normal consistency and a good workability according to the flow table test as established in UNE 83-811-92 (1992). The mixtures were moistened by spraying with the optimum w/c ratio and then placed in steel moulds to obtain prismatic test specimens of 40 × 40 × 160 mm, as described in EN 196-1 (2016).

2.2. Methods

Ilmenite mud samples, OPC, and the new cements obtained were physico-chemically characterised through the identification of the mineral phases by the X-ray diffraction (XRD) technique in a Shimadzu diffractometer model XRD 6000, using Cu K α radiation working at 1.2 kW (40 kV e 30 mA). Data were recorded in the 5-60° 2 θ range (step size equal to 1°/minute). The quantification of major elements was carried out 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. Trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) using an HP branded computer model HP4500®. The system was previously calibrated with the appropriate standards. In addition, the particle size distribution was studied 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. Then, the properties of the obtained cements were compared with the properties of OPC. The consistency and setting times were calculated using a Vicart apparatus and the soundness by Le

Chatelier's method as established in EN 196-3 (2017). The heat of hydration was studied according to the calorimetric test as established in EN 196-9 (2011). Drying shrinkage analysis was applied in accordance with the norm ASTM C 596-09 (2017). The mechanical resistances and flexural and compression strengths were determined in mortar after 2 and 28 days according to EN 196-1. The mortar was prepared as described in EN 480-1 (2015). Finally, the new cements were characterised from an environmental perspective. The TCLP leaching test was performed to assess the environmental risks. Moreover, the radionuclide activity concentrations were measured by high-resolution low-background gamma spectrometry with high-purity germanium detectors (HPGe). In addition, the concentrations of both thorium and uranium isotopes and ^{210}Po were determined by the alpha spectrometry technique with ion-implanted Si detectors (PIPS detectors) (Lozano et al. 2011; Hurtado et al. 2003). Furthermore, the radiological implications were studied according to Index I and Ra equivalent indexes. The analyses were carried out in accredited laboratories and the required quality control was performed by taking periodic blanks, certified reference materials, and replicates and participating in national and international inter-comparison exercises.

3. Results and Discussion

3.1. Materials characterisation

Figure 1 shows the grain-size distribution of both the ilmenite mud and the OPC samples used in this study, revealing an asymmetric distribution with a wide range of particle sizes. Two relative maxima were observed for OPC (Fig. 1), with the main fraction being around $30\ \mu\text{m}$ and the second one around $6\ \mu\text{m}$. According to the particle size of the OPC, the optimal size of the additives should be smaller than $40\ \mu\text{m}$. Around 75% of the particles present in the ilmenite mud are below $40\ \mu\text{m}$ (Fig. 1).

The chemical compositions of the raw materials (ilmenite mud and OPC) are shown in Table 1. The ilmenite mud waste shows a relatively large amount of elements expressed as oxides, such as TiO_2 (53 wt.%), SiO_2 (12 wt.%), and Fe_2O_3 (12 wt.%). Moreover 7.8 wt.% SO_3 and 2.3 wt.% ZrO were found (Gázquez et al. 2011; Contreras et al. 2013, 2014). With regard to the main trace elements identified in the ilmenite mud, some of them are present in high concentrations compared to a typical soil (V, Nb, Cr, Cu, Pb, Zn, La, and As), while others are found in lower concentrations (Sr, Sn, Co, Ni, and Cd) (Rudnick and Gao 2003). The major components of the cements were Ca (CaO , 63 wt.%) and Si (SiO_2 , 20 wt.%), while Al, S, and Fe were present in lower concentrations (Al_2O_3 : 6.2 wt.%; SO_3 : 2.8 wt.%; and Fe_2O_3 : 2.3 wt.%).

In accordance with the mineralogical analysis (Fig. 2a), the crystalline components of the ilmenite mud were unattacked ilmenite (FeTiO_3), rutile (TiO_2), and residual fractions of zircon (ZrSiO_4), quartz (SiO_2), and Fe-Ti oxides ($\text{Fe}_3\text{Ti}_3\text{O}_{10}$); these results are in agreement with those of previous works (Gázquez et al. 2011; Contreras et al. 2013, 2014). In addition, as expected, alite (C_3SiO_5) and belite (C_2SiO_4) are the major minerals phases of Portland cement (Fig. 2b). Moreover, typical minority phases such as tricalcium aluminate ($\text{C}_3\text{Al}_2\text{O}_6$), tetra calcium ferro-aluminate (C_4AlFe), gypsum ($\text{CaSO}_4(\text{H}_2\text{O})_2$), and hemihydrate ($\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$) were detected. Figure 3 shows the XRD patterns of the cement paste with different ilmenite mud additions after 28 days. When comparing these patterns with the commercial cement pattern (Fig. 2b), as a consequence of the hydration reactions of the cement, the XRD peaks associated with the presence of alite decrease in intensity and new peaks associated with the formation of portlandite and ettringite appear (Fig. 3). The alite (C_3SiO_5) reactions with water produce C-S-H and calcium hydroxide, $\text{Ca}(\text{OH})_2$ (also known as portlandite). In addition, ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) is formed as a consequence of the reaction of the tricalcium aluminate (C_3A) with the presence of sulphates from gypsum and the residual sulphur present in the ilmenite mud, which is used as setting retardant. However, the intensity of the ettringite peaks increases with the percentage of ilmenite mud, probably due to its sulphate content. Moreover, with the addition of ilmenite mud to the cement, the presence of the peaks associated with rutile is observed. The intensity of the rutile peaks increases with the amount of ilmenite mud added. This indicates that the majority of the ilmenite mud acts as an inert component, not forming new crystalline phases (Fig. 3), a fact that is expected since it is formed by very refractory minerals.

3.2. Technological properties

In Table 2, the technical properties of the IMCs are shown and compared with OPC. The consistency was evaluated according to the water/cement (w/c) ratio as establishes the EN 196-3 (2017), obtaining values of about 0.26–0.28, typical of commercial cement paste. The addition of ilmenite mud increased the optimum w/c ratio slightly. Moreover, these w/c ratios increase with the percentage of ilmenite mud and were similar to the reference material (OPC) value (Table 2). The addition of ilmenite mud increases slightly the amount of water needed to manufacture the final cement.

The setting time improves slightly with the addition of up to 10 wt.% mud (Table 3). All the values obtained are in accordance with the initial ($\geq 45\ \text{min}$) and final ($\leq 720\ \text{min}$) setting time values established in the

European regulation EN 196-3. This result shows that the addition of ilmenite mud increases the initial time of setting slightly but significantly reduces its duration, indicating that the ilmenite mud acts as inert material. For example, in the IMC2.5 (2.5% IM) and IMC5 (5% IM) samples, the total setting times are 43 and 45 minutes respectively, 50 and 59% lower than the setting time of the commercial cement taken as reference. The obtained results are in accordance with previous studies carried out with titanium dioxide nanoparticles (Atta-ur-Rehman et al, 2018; Nazari and Riahi 2011a).

The soundness was studied according to the expansion of the cements by the procedure established in EN 196-3. It is essential that the cement paste does not undergo any appreciable change in volume after setting, since such a change could cause cracks, undue expansion, and as a result disintegration of concrete. The results were in accordance with the standards (maximum expansion of 10 mm) and mud does not introduce relevant modifications compared with cement paste based only on commercial Portland cement (Table 3). In addition, IMC2.5 reduces the expansion in relation to OPC, which is advantageous.

The values for the heat of hydration determined in accordance with EN 196-9 (2011) are also shown in Table 3. The total heat released as a function of time decreases slightly with the percentage of ilmenite mud, which is expectable from the high proportion of refractory minerals contained in the mud. The results ranged from 220 to 227 J g⁻¹ at 41 h, and consequently the cements are classified as having low heat of hydration according to the standard limit (< 270 J g⁻¹). Similar values were found in a previous study with a similar waste (Bobrowicz J., Chylinski, 2016). Moreover, all IMCs showed lower heat of hydration than the reference cement (OPC). For example, the value for IMC2.5 (220.0 J g⁻¹) is 13.5% lower than that for OPC (254.3 J g⁻¹), confirming that mud does not generate several additional hydration chemical reactions. This fact can be advantageous in large civil works, such as dams, in which huge amounts of cement are demanded, since the heat released is quite important.

The resistance of the cements studied was evaluated on a mortar prismatic specimen according to EN 196-1 (2005). The flexural strength of specimens containing up to 10 wt.% mud were studied after 2 and 28 days (Table 4). IMC5 had compressive strengths similar to those of OPC mortars. Furthermore, the addition of 2.5 wt.% ilmenite mud improves the compressive strength slightly after 2 days of curing compared to the reference cement. This increase in resistance after 2 days of curing may be positive in the pre-manufactured industry, because the specimens can be demoulded before 48 hours. Moreover, the values obtained for the cements after 2 and 28 days containing up to 5 wt.% ilmenite mud were in agreement with the minimum values required in EN 196-1. On the other hand, the flexural and compressive resistances decreased for the IMC10 in relation to OPC reference mortar. The results are in accordance with previous studies showing that more than 5 wt.% TiO₂ reduces the resistance (Katyal et al. 1999a, b; Atta-ur-Rehman et al, 2018).

The standard test method for drying shrinkage of mortar containing Portland cement was applied according to ASTM C 596-09 (2017). This test method covers the determination of the change in length on drying due to the moisture gradient that exists between the inside and outside of the sample. This differential water loss can cause a change in the volume of the cement paste, causing cracks. According to the resistance of the cements, lower values of linear retraction are advantageous to avoid internal defects such as cracking or other similar faults during the drying process. The drying shrinkage showed that the addition of ilmenite mud reduced the shrinkage and deformation of the material during the drying process. This is probably due to the fact that the ilmenite mud particles occupy the pores, improving the stability of the cement compared with reference material (OPC) (Fig. 4). In addition, as the hydration time advances, the shrinkage remains constant in all the samples until the final curing process (28 days). However, the shrinkage values obtained in all the samples studied are within the limits established by the standard (ASTM C 596-09).

3.3. Environmental study

Since ilmenite mud is classified as NORM, it was necessary to carry out a deep radiological characterisation. Table 5 shows the results of the radioactive characterisation of the ilmenite mud, OPC, and cements containing mud (IMCs). The ilmenite mud shows a ²²⁸Ra concentration (2580 Bq kg⁻¹) higher than the safety threshold (1000 Bq kg⁻¹) for NORM established by the IAEA (2004) as well as significant activity concentrations of both ²²⁶Ra and ²²⁸Th (520 and 704 Bq kg⁻¹, respectively). Similar results were obtained in previous works (Gázquez et al. 2009a, b, 2011; Contreras et al. 2013, 2014). These concentrations are significantly higher than the average worldwide values for soils (35 Bq kg⁻¹ of ²³⁸U and ²³²Th in secular equilibrium with their daughters), revealing that the radionuclide concentrations in the OPC are similar to those of unperturbed soils (UNSCEAR 1993).

In order to evaluate this problem, the I index, called the activity concentration index, is used to ensure that the external gamma dose does not exceed 1 mSv per year for building materials laid down in Article 75(1) of the 2013/59/EURATOM council directive, according to the following equation:

$$I = \frac{C_{226Ra}}{300 \text{ Bq/kg}} + \frac{C_{228Ra}}{200 \text{ Bq/kg}} + \frac{C_{40K}}{3000 \text{ Bq/kg}} \quad [\text{Eq. 1}]$$

where $C^{226}\text{Ra}$, $C^{228}\text{Ra}$, and $C^{40}\text{K}$ are the activity concentrations for ^{226}Ra , ^{228}Ra , and ^{40}K , respectively, expressed in Bq kg^{-1} .

This index should not exceed the value of unity ($I \leq 1$) for materials used in bulk amounts such as concrete or $I \leq 6$ for surface materials and those with restricted use, e.g. tiles, boards, etc., to ensure that the additional external dose received by occupants living in buildings constructed with these materials does not exceed the reference value of 1 mSv year^{-1} (2013/59/EURATOM). Table 5 shows that index I is lower than one for IMC2.5 and IMC5 materials. This makes the ilmenite mud a suitable material for use as additive (up to 5 wt.%) in cement manufacturing without radiological implications. Nevertheless, the IMC10 could have other civil construction applications, for example, in marine platforms or bridges, since its radiological impact on the environment is negligible, as shown below. Furthermore, any IMC could be used as mortar (usually the cement/sand ratio is 1/3), since the sand shows a low radioactivity content (about 5 Bq kg^{-1} of Th and U) and the activity concentration of any cement is reduced three times; consequently the index I would be below one.

Furthermore, another common radiological index has been introduced to evaluate the actual activity level of ^{226}Ra , ^{232}Th , and ^{40}K in the samples and the radiation hazards associated with these radionuclides. This index is usually known as the radium equivalent activity (Ra_{eq}) (Beretka et al. 1985; Ahmad et al. 1988; Ravisankar et al. 2012).

$$Ra_{(eq)} = C_{226Ra} + 1.43 \cdot C_{228Ra} + 0.077 \cdot C_{40K} \quad [\text{Eq. 2}]$$

where $C^{226}\text{Ra}$, $C^{232}\text{Th}$, and $C^{40}\text{K}$ are the activity concentrations of ^{226}Ra , ^{232}Th , and ^{40}K respectively. In the definition, it is assumed that 370 Bq kg^{-1} of ^{226}Ra , 259 Bq kg^{-1} of ^{232}Th , and 4810 Bq kg^{-1} of ^{40}K produce the same equivalent dose rate (Krisiuk et al. 1971; Stranden 1979). The values of calculated $Ra_{(eq)}$ are shown in Table 5. The calculated $Ra_{(eq)}$ values ranged from 171 Bq kg^{-1} (IMC2.5) to 484 Bq kg^{-1} (IMC10). In cements containing up to 5 wt.% ilmenite mud, the values of the $Ra_{(eq)}$ are found to be lower than the criterion limit of 370 Bq kg^{-1} (Kovler 2009; NEA-OECD 1979), and as such they do not pose a radiological hazard when used as bulk materials in building constructions.

Finally, a TCLP leaching test was applied to evaluate the potential environmental impact generated by hazardous metals contained in the cements studied (U.S. EPA. 1997). According to the TCLP test (Table 6), the values obtained are clearly below the limits given by the U.S. EPA (2011). Moreover, it is concluded that contaminants in the ilmenite mud are immobilised in the cementitious matrix. This is reflected in the lower leaching values obtained in the ilmenite mud for iron and titanium: concentrations of $3 \mu\text{g kg}^{-1}$ of Ti and below $1 \mu\text{g kg}^{-1}$ of Fe.

Furthermore, the European Commission Directive 2003/53/EC prohibits the supply or use of cement which has a chromium VI concentration of more than 2 parts per million of cement (2 mg kg^{-1} of cement). As well as cement itself, the restriction applies to a wide range of products that contain cement such as mortars, grouts, tile adhesives, and so on. This legislation is being introduced to help prevent allergic contact dermatitis, a potentially serious condition that can lead to permanent disability, which can occur when wet cement containing chromium VI comes into contact with the skin. According to the Cr results (see Table 6), and taking into account that for the TCLP test a dilution factor of 20 has been applied, a total chromium content in the range of $1.4\text{--}1.7 \text{ mg kg}^{-1}$ is obtained. Assuming the most unfavourable situation in which all leached chromium is chromium VI, the values obtained are below the limit of 2 mg kg^{-1} (Directive 2003/53/EC).

On the other hand, the radionuclide contents of the liquid fractions obtained in the TCLP test were also analysed by alpha spectrometry (Table 7). The activity concentrations are fairly low and similar among the samples and the reference material (OPC). These results show that radionuclides are immobilised and almost none leached out from the cementation matrix. In addition, the concentration of U-isotopes was clearly below the guideline value for uranium in drinking water ($10 \text{ Bq}\cdot\text{L}^{-1}$) introduced by the World Health Organisation (WHO) 2015 and lower than the typical range of $0.005\text{--}0.5 \text{ Bq}\cdot\text{L}^{-1}$ for continental waters (Mas et al. 2006). Moreover, the concentrations of Th-isotopes showed lower values in leaching of IMC10 ($0.005 \text{ Bq}\cdot\text{L}^{-1}$ of ^{232}Th) and the maximum value was $0.121 \text{ Bq}\cdot\text{L}^{-1}$ of ^{230}Th in leaching of OPC. These results were of the same order of magnitude as typical ones in continental waters (Mas et al. 2006), and lower than the guidance levels for thorium radionuclides in drinking waters ($1 \text{ Bq}\cdot\text{L}^{-1}$) (WHO 2015).

According to the results, the activity concentrations in leaches were quite low and were lower than the representative worldwide average and guidance level; therefore, there would be a negligible environmental impact and a negligible effective dose equivalent received by the public.

4. Conclusions

The present study has demonstrated that ilmenite mud from the TiO₂ industry can be successfully valorised by including it as an additive in the manufacture of Portland cements, since these cements satisfy the regulations related to both technological properties of OPC and environmental constraints.

- The XRD analysis showed that no significant effects on the crystalline phases were observed as a consequence of the hydration reactions of the cement with the addition of ilmenite mud, but ettringite formation was helped.
- There were no significant effects on the strength compared to OPC with the addition of up to 5 wt.% ilmenite mud. Moreover, IMC2.5 has better properties after 2 days of curing than the reference material, reducing the porosity and improving the compressive strength.
- The addition of up to 10 wt.% mud delays the initial setting time in relation to OPC.
- Ilmenite mud increases the volume stability of the final cement during the drying stage and reduces the deformation of the final material.
- The heat of hydration decreases slightly with the percentage of mud due to the refractory minerals contained in the mud.
- The radioactivity concentration indices showed that IMC2.5 and IMC5 could be used as bulk construction materials with very low environmental risk. Although not suitable for the construction of occupied buildings, IMC10 in particular could be safely used in concrete construction works.
- Finally, the leaching experiments demonstrated a negligible mobility of metals and natural radionuclides, and consequently the use of these IMC cements will produce a negligible environmental impact.

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Figure Captions

Fig. 1. Particle size distribution analysis (a) distribution density and (b) under cumulative distribution of ilmenite mud (MUD) and commercial cement (OPC).

Fig. 2. XRD patterns of (a) ilmenite mud and (b) ordinary Portland cement (OPC).

Fig. 3. XRD patterns of the manufactured cement pastes at 28 days.

Fig. 4. Drying shrinkage test of the ordinary Portland cement and the manufactured cements.

Table captions

Table 1. Chemical composition analysis of major elements (wt.%) and trace elements (mg kg^{-1}) of the ilmenite mud (MUD) and ordinary Portland cement (OPC) used. L.O.I. (Loss on Ignition).

Table 2. Optimum w/c ratio in cement pastes and mortars.

Table 3. Optimum W/C ratios, setting times, soundness, and heat of hydration of the IMC and OPC pastes.

Table 4. Flexural and compressive strengths (MPa) of the IMC and OPC mortars after 2 and 28 days of curing.

Table 5. Activity concentrations (Bq kg^{-1}) of ilmenite mud (MUD), ordinary Portland cement (OPC), and the cements mixtures (2.5, 5, and 10 wt.% mud). The external risk rate I and $R_{a(\text{eq})}$ were calculated.

Table 6. Leachability concentrations of metals ($\mu\text{g L}^{-1}$) obtained by TCLP test from the IMC10 sample and reference material (OPC) measured by ICP-OES. Liquid 1 is the fluid extractant used in the TCLP test.

Table 7. Average concentration (mBq L^{-1}) of each sample analysed by alpha spectrometry. Liquid 1 is the fluid extractant used in the TCLP test.