



## Valorisation of ilmenite mud waste in the manufacture of commercial ceramic



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### HIGHLIGHTS

- Environmentally friendly ceramics were manufactured using waste ilmenite mud.
- First time that ceramics are manufactured by using mud from ilmenite.
- The new ceramics present better technological properties than commercial ceramics.
- The use of this waste produces negligible environmental impacts.

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### ABSTRACT

This paper reports the results of a study focused on the production of ceramic tiles from ilmenite mud (MUD), a waste generated by the industry devoted to the TiO<sub>2</sub> pigment production. Ceramic tiles were produced from mixtures of a commercial red stoneware mixture (RSM) with different concentrations of mud (3, 5, 7, 10, 30 and 50 wt.%). The samples were sintered to simulate a fast-firing process. The sintering behaviour of the fired samples was evaluated according to ISO methodologies by linear shrinkage, water absorption and porosity measurements. Both green powder and fired samples were characterised by means of X-ray diffraction (XRD), differential scanning calorimetry (DSC/TG), field emission scanning electron microscopy (FESEM) and bending strength measurements. Moreover, since this activity is a NORM (Naturally Occurring Radioactive Material) industry, the radionuclides activity concentrations were measured by both gamma and alpha spectrometry techniques. Finally, the TCLP leaching test (Toxicity Characteristic Leaching Procedure, USEPA) was performed to assess the risks of the use of undissolved mud tiles from an environmental perspective. The results obtained demonstrated that ilmenite mud can be successfully valorised in the manufacture of red stoneware ceramic bodies, with even better technological properties than commercial ones. The addition of mud as additive (from 3% to 10%) had a beneficial effect to the sintering processes, improving the bending strength (up to 15%) and reducing both apparent porosity and water absorption (up to 50%).

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## 1. Introduction

Because of the depletion of natural resources, increasing greenhouse emissions and awareness of the need for sustainable development in terms of safe reuse of wastes, the transformation of these

wastes into valuable materials (i.e. valorisation) is emerging as a strong trend. In this context and taking into account the growing awareness of the need for protection of health and environment, the recovery of wastes currently generated in most industrial processes is the subject of a thorough investigation [1–3]. The valorisation of wastes as secondary raw materials in the manufacture of construction materials could allay the problems associated with both the depletion of natural resources and the disposal of industrial wastes [4–7]. In this context the protection of health and environment is of great importance, although the economic benefits accruing from waste recycling must not be ignored [8,9].

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This work is mainly focused on the recovery of waste generated by the titanium dioxide pigment industries.  $\text{TiO}_2$  production begins with the mixing of ilmenite ( $\text{Fe}_2\text{TiO}_3$ ) with highly concentrated sulphuric acid (80–95%) [10]. The liquor generated goes to a clarification tank where the un-attacked solid – ilmenite mud (MUD) – is allowed to settle. Then this mud is separated from the liquor by a process of decantation and filtration, and finally stored in a safety area. The magnitude of this generated waste is around 30,000 tons per year, which until now have not had any use, and therefore it is disposed of in an authorised waste repository [11]. Moreover, the content of natural radionuclides is high in relation to a typical soil (about 100 times higher), and so it is classified as a NORM (Naturally Occurring Radioactive Material) industry, which presents enhanced levels of radionuclides from the natural uranium and thorium series.

This waste has been classified by the competent authorities as “hazardous waste”, according to the European legislation (Commission Decision 2000/532/EC as amended three times by the Commission Decisions 2001/118/EC, 2001/119/EC and 2001/573/EC). Therefore now this is stored in a controlled landfill repository, which implies a cost of about three million euros for its final elimination (including transportation costs). Therefore, if this waste could be valorised a significant improving in the competitiveness of this industry will be produced.

In this context, a correct environmental solution to the disposal of a wide range of solid wastes could be their incorporation into ceramics [12,13]. The prospective benefits of using ilmenite mud as an additive in tile manufacture include immobilising some heavy metals and radionuclides in the final matrix, oxidising organic matter and destroying any pathogens during the firing process, as well as reducing frost damage, based on the results of several full- or bench-scale studies [14–16]. In addition, there is no costs in incorporating this waste like additive in ceramics production, depending the saving on the fraction of waste added to each tile and the costs of the transportation of the waste from into the ceramic plant. Therefore, as average we think that no additional costs will be involved in the use of this waste for ceramic manufacturing.

Taking into account the mud's composition [16–18], it is essential to study whether the presence of this residue modifies the mechanical properties of the new ceramic tile through a physico-chemical analysis (elemental, mineralogical and morphological) of the wastes and raw materials used in the generation of the tile tested. In addition, it is essential to check its environmental impact in relation to the potential problem of leaching of metals and radionuclides included in the ceramic matrix.

Taking in consideration the previously established problem, the main objective of this work was to analyse the option of producing ceramic tiles with different ilmenite mud waste proportions and compare it with a standard commercial ceramic, studying its technological properties and the environmental implications.

## 2. Materials and methods

### 2.1. Materials and sample preparation

The ilmenite mud was previously dried in an oven at 110 °C for at least 48 h until constant weight, and then grounded and sieved to a particle size >160  $\mu\text{m}$ . As it will be discussed further, the ilmenite mud is characterised by a high content of iron oxide ( $\text{Fe}_2\text{O}_3 = 10\%$ ). For that reason, its valorisation in ceramic tile has been achieved through its incorporation into a composition of red stoneware, which is made from natural clays with high iron oxide content ( $\text{Fe}_2\text{O}_3 > 7\%$ ). Several mixtures with red stoneware (RSM [code sample 100/0]; supplied by Tierra Atomizada, S.A.) and different concentrations of ilmenite mud (3%, 5%, 7%, 10%, 30% and 50%, code samples 97/3, 95/5, 93/7, 90/10, 70/30 and 50/50 respectively) were prepared. The mixtures moistened by spraying with distilled water (6 wt.%) and then shaped by uniaxial pressing (Nannetti S hydraulic press) at 40 MPa in a steel die, to obtain tiles measuring 50 × 50 × 5 mm. These tiles were fired in an electric furnace at 1150 °C for eight minutes following the fast-firing process recommended by the red stoneware supplier (Fig. 1).

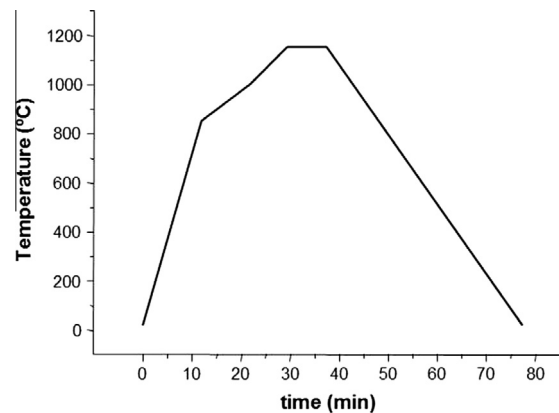


Fig. 1. Heating cycle used for the fast-firing of ceramic tiles.

### 2.2. Characterisation techniques

The identification of the mineral phases was performed by the XRD technique (X-ray diffraction) which applied the method of dust lost in a Bruker diffractometer (model D8 Advance), using  $\text{Cu K}\alpha$  radiation excited by a current of 30 mA and a voltage of 40 kV. Data were recorded in the 5–70°  $2\theta$  range (step size 0.019736° and 0.5 s counting time for each step).

The measurement of major elements and trace elements was performed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry), using an HP branded computer model HP4500® and by ICP-OES (Inductively Coupled Plasma Optical Emissions Spectrometer) using a Jobin Yvon ULTIMA 2. Both systems were previously calibrated with the appropriate standards.

The microstructure of tiles was examined by field emission scanning electron microscopy (FESEM) (HITACHI model S-4800) operating at 20 kV. SEM specimens were polished with 6, 3 and 1  $\mu\text{m}$  diamond pastes after grinding with silicon carbide paper and water and subsequently Au–Pd coated in a Balzers SCD 050 sputter.

The thermal behaviour of the raw materials (ilmenite mud and RSM) and all the mixtures were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (SETARAM model Labsys) on powder samples (size particle = 80–100  $\mu\text{m}$ ). DSC/TGA scans were performed between 25 °C and 1450 °C at 50 °C/min in flowing air, platinum crucibles and calcined  $\text{Al}_2\text{O}_3$  as reference material. The DSC/TG curves were normalised regarding the sample weight.

### 2.3. Technological characterisation

The sintering behaviour of tiles was evaluated on the basis of water absorption, apparent porosity and bulk density. The water absorption was measured according to EN ISO 10545-3 [19] for ten representative specimens. The water absorption coefficient,  $E$  (dry wt.%), was calculated by the equation:

$$E = \frac{(m_2 - m_1)}{m_1} \times 100 \quad (1)$$

where  $m_2$  (g) is the mass of wet specimen and  $m_1$  (g) is the mass of dry specimen.

The apparent porosity and the bulk density were measured according to ASTM C373-88 [20], which involves drying the test specimens to constant mass ( $D$ ). The test was carried out on ten representative specimens. After impregnation, the mass ( $S$ ) of each specimen while suspended in water and their saturated mass ( $M$ ) was determined. The apparent porosity,  $P$  (%), expresses the relationship of the volume of open pores with the exterior volume of the specimen and is calculated as follows:

$$P = \frac{(M - D)}{(\rho \cdot V)} \times 100 \quad (2)$$

where  $V$  ( $\text{cm}^3$ ) is the exterior volume ( $V = M - S$ ) and  $\rho$  is the density of the water 1  $\text{g cm}^{-3}$ .

The bulk density,  $B$  ( $\text{g cm}^{-3}$ ), of a specimen is the quotient of its dry mass divided by the exterior volume, including pores:

$$B = D/V \quad (3)$$

Linear shrinkage, LS (%), was calculated by the equation:

$$LS = \frac{(L_i - L_f)}{L_i} \times 100 \quad (4)$$

where  $L_i$  (mm) is the specimen length without firing and  $L_f$  (mm) is the specimen length after firing.

Bending strength, BS (MPa), was measured according to EN 843-1 [20] in an electronic universal tester (Servosiv model ME-402/01) on ten test specimens for each sintered temperature by a three-point loading test with a span of 32 mm and a crosshead speed of 1 mm/min.

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