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Research paper

Ceramic porcelain stoneware production with Spanish clays purified by means of the removal of iron compounds and organic matter using physical methods

E. Barrachina*, I. Calvet, D. Fraga, J.B. Carda

Department of Inorganic and Organic Chemistry, Universitat Jaume I, Castellón, Spain

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ABSTRACT

As the production of ceramic porcelain stoneware in Spain is totally conditioned by the importation of ball clays, because of the lack of adequate Spanish ball clays, this work has focused on the formulation of ceramic porcelain body from Spanish clays purified by means of physical removal processes. This method was applied to three Spanish clays containing common clay impurities of iron (hematite and siderite) and organic matter. Iron removal was carried out using the wet sieve method, the hydrocycloning method and the electromagnetic filtering method, obtaining a reduction in iron content of up to 80 wt%, while the clay containing organic matter was treated thermally at 400 °C for 30 min so as to leave it almost completely purified. These treated clays, after being characterized (chemical and mineralogical composition, plasticity, organic carbon, thermal behaviour and colour), were used in the porcelain stoneware body composition instead of imported clays, the result being a composition capable of substituting the standard porcelain stoneware formulation in terms of sintering, morphology, colour, flexural strength and dilatometry.

1. Introduction

In Spain, the white clays rich in kaolinite, so-called ball-clays, usually employed in white porcelain stoneware bodies because they confer strength and plasticity are mostly imported from other countries such as Ukraine, France, Germany or United Kingdom, due to the lack of appropriate quality of Spanish ball clays. In this regard, some Spanish kaolinitic clays, from the regions of Teruel and Ciudad Real, both of which are very near the province of Castellón, where the Spanish ceramic cluster is situated, are included in porcelain compositions, but in limited amounts. Typical clay impurities that are frequently found include pyrite, siderite, organic matter, iron and titanium oxides and their quantity, form and type can influence the usefulness, processing route and ceramic application of each clay (Barba et al., 2002; Bauluz et al., 2008; Carda and Sánchez, 2003; Jordán et al., 2015; Kogel et al., 2006; Sánchez et al., 2004; Sanfeliu and Jordán, 2009).

The argillaceous minerals, such as these clays, contain substantial amounts of carbon and organic materials, sulphur and its compounds, and some oxides of transition metals (particularly iron) which can generate defects in the sintered ceramic products in their lower valence state (Romero and Pérez, 2015). The excess of organic matter in clays, due to the usual fast firing cycle in porcelain stoneware production, can cause the presence of a typical fault in ceramic tiles called "black core", which is formed by carbon residues from the thermal decomposition of the organic material contained in the clays (Abdrakhimov and Abdrakhimova, 1999; Maritan et al., 2006). The incomplete oxidation during the firing phase results in certain products being burnt in the ceramic product, and causes certain textural changes (and imperfections), which lowers the quality of the ceramic products and the mechanical resistance characteristics of the final product (Da Silva et al., 2000). As a slow firing cycle is not practical in industry, clays containing organic matter are not commonly employed in the formulation of porcelain bodies. The methods proposed to reduce the amount of organic matter consist in increasing the oxidising atmosphere and pretreating the clay with a thermal route in order to decompose the organic matter, before it is used in the ceramic formulations (Baraldi and Zannini, 2014; Barba et al., 2002; Carda and Sánchez, 2003; Lores et al., 1997).

Although standard UNE-EN 14411:2013 does not establish the Fe_2O_3 content in porcelain body, in the ceramic sector it is known that the $\%Fe_2O_3$ measured by X-ray fluorescence (XRF) must be < 1 wt% (Fraga et al., 2016; Sánchez et al., 2010). Consequently, the clays used in porcelain stoneware tile formulation commonly should contain < 1 wt% Fe_2O_3 (Dondi et al., 2014; Galos, 2011). Some of the Spanish

* Corresponding author.
E-mail address: ebarrach@uji.es (E. Barrachina).

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sedimentary clays located in deposits in Teruel and Ciudad Real, however, present high percentages of iron compounds as impurities, thus restricting their use in the formulation of the white body of porcelain stoneware tiles (Barba et al., 2002). This paper presents a method for improving three Spanish clays containing impurities of iron compounds and organic matter in their original state, by means of physical methods. After removal of the impurities, the treated clays were used to replace some imported ball clays in the porcelain body composition, the result being a new formulation exhibiting the same properties as the standard reference.

2. Geological setting

The study area is located in two Spanish provinces: Teruel (NE Spain) and Ciudad Real (Southern central Spain). The clayey rocks, shallow type, from Teruel were formed due to the continuous floods to which the peat-bogs were submitted, according to the sedimentary model of "Escucha" formation. The main impurities of these clays are organic matter and siderite ($FeCO_3$). The clays from Ciudad Real, however, have their origins in sedimentary kaolins of the paleozoic levels and they are also considered altered slate rocks, exhibiting a very low degree of metamorphism and containing mainly kaolinite, muscovite and pyrophyllite (Galán and Martín, 1974; García and Martínez, 1992; Juan et al., 1993; Lores et al., 1997; Parra, 1996).

3. Materials and methods

One clay from Ciudad Real (CR-01) and two clays from Teruel (TE-01 and TE-02) were analysed: the clay from Ciudad Real (CR-01 clay) had hematite (Fe_2O_3) as its main impurity, while TE-01 clay was rich in organic matter and TE-02 clay contained siderite.

The physical treatment to reduce the organic matter content consisted in the firing the clay method (FCM), after previously being dried and crushed, at different temperatures (range: 250 °C–600 °C with 30 min of residence time) in order to decompose the organic matter to be removed.

The methods proposed in the current paper to remove the iron compounds in these Spanish clays are physical methods, in contrast to the numerous chemical methods and patents studied in other papers (Ambikadevi and Lalithambika, 2000; Asmatulu, 2002; Cameselle et al., 1995; Council et al., 2000; González and Del, 2006; Murray, 2007; Ramaswamy, 2007; Toro et al., 1993; Zegeye et al., 2013). The reason underlying this decision was that, because they do not include the addition of chemicals, they are more manageable processes for the ceramic industry. The reduction of the amount of iron compounds was also carried out by means of three physical methods: (1) the wet sieving method (WSM) was used to remove the coarse fraction: the clay was mixed with water in a mechanical stirrer until it became a suspension with a slurry density of 1.50 g/cm^3 (Fig. 1). The suspension fluidity was improved by adding 0.5 wt% of deflocculant (sodium silicate). (2) The hydrocyclone method (HCM) was implemented on a clayey slurry with an inlet working pressure of 1.5 bar and a density of 1.25 g/cm^3: when the slurry enters through the feed tangential inlet (a), cycloning starts to take place in the feed chamber (b). Then, the heavier particles move to the outer walls and towards the apex (c), while the lighter particles stay near the centre of the cone and are carried away by the vortex finder (d), Fig. 1 (911 Metallurgy Corporation, 2016). (3) The electromagnetic filter method (EFM) uses a non-permanent magnet capable of producing a 2500-Gauss magnetic field. The removed hematite, together with a small quantity of finer clay particles, are stuck to the electromagnetic filter, which must be cleaned before beginning each new operation (Fig. 1). The conditions of the slurry to be filtered were: flow of 1.5 l/min and a density of 1.38 g/cm^3. These devices are usually utilised in the removal of impurities in minerals such as clays, kaolin, feldspar, glass, etc. (Al-Momani and Khoury, 2010; Bradley, 2013; Khramov and Sokolov, 1956; Rao and Vibhuti, 2004; Scott and Bristow, 2002).

The main purpose of these treated Spanish clays is to substitute the clays imported from Ukraine used in the porcelain stoneware body compositions shown in Table 1. The raw materials are as follows: TE-01, clay from Teruel rich in kaolinite and with organic matter as an impurity; TE-02, clay from Teruel rich in siderite; CR-01, clay from Ciudad Real rich in kaolinite and with the presence of hematite; CY-01 and CY-02, clays from Ukraine rich in kaolinite and free of impurities; FD-01 sodium feldspar from Turkey; FD-02, sodium-magnesium feldspar from Sardinia; and FS, feldspathic sand. The first composition is the standard one (STD), for a typical porcelain stoneware body, formulated exclusively with Ukrainian clays used as the reference composition; composition A is a reformulation of STD using Spanish clays without treatment; composition B is a modification of A, but using the treated Spanish clays.

Each composition was micronised in a planetary mill with water and 0.7 wt% of deflocculant (sodium silicate) at a suspension density of 1.70 g/cm^3 and sieved at under 100 μm. To simulate industrial pressing

Table 1
Detailed formulation of porcelain compositions based on Spanish treated clays (wt%).

Raw materials	STD	A	B
TE-01 (organic matter)	**–**	**10**	**–**
TE-02 (siderite)	–	5	–
CR-01 (hematite)	–	10	–
TE-01 after treatment	**–**	**–**	**10**
TE-02 after treatment	**–**	**–**	**5**
CR-01 after treatment	**–**	**–**	**10**
CY-01	20	10	10
CY-02	25	15	15
FD-01	35	25	25
FD-02	10	15	20
FS	10	10	5

The treated clays are underlined in bold.

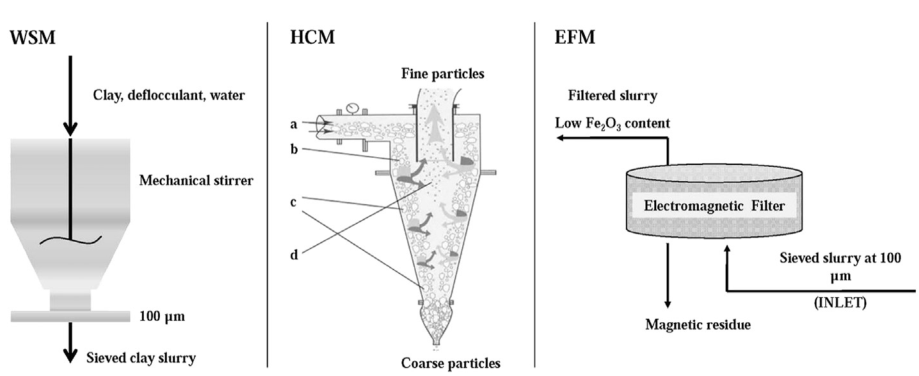

Fig. 1. Diagrams of the physical methods used to remove iron compounds from clays: WSM, wet sieving method; HCM, hydrocycloning method; EFM, electromagnetic filter method.