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)
ebarrach@uji.es

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 minutes 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.

KEYWORDS

Clay, impurity, iron, organic matter, ceramic porcelain stoneware tiles
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, 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 pre-treating 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$_2$O$_3$ content in porcelain body, in the ceramic sector it is known that the %Fe$_2$O$_3$ measured by X-ray fluorescence (XRF) must be less than 1 wt% (Fraga et al., 2016; Sánchez et al., 2010). Consequently, the clays used in porcelain stoneware tile formulation commonly should contain less than 1 wt% Fe$_2$O$_3$ (Dondi et al., 2014; Galos, 2011). Some of the Spanish 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 was 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 ($\text{Fe}_2\text{O}_3$) 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: 250ºC-600ºC with 30 minutes 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.). 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. (91 Metallurgy Corporation, 2016). (3) The electromagnetic filter method
(EMF) 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.

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

<table>
<thead>
<tr>
<th>RAW MATERIALS</th>
<th>STD</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE-01 (organic matter)</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>TE-02 (siderite)</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>CR-01 (hematite)</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>TE-01 after treatment</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>
Each composition was micronised in a planetary mill with water and 0.7 wt% of defloculant (sodium silicate) at a suspension density of 1.70 g/cm$^3$ and sieved at under 100 micrometres. To simulate industrial pressing conditions, the compositions were homogenised and moistened with water to 6.5 wt% to be pressed in a uniaxial laboratory press (Nannetti), resulting in rectangular pieces. After having been dried at 110°C for 24 h, the pieces were fired at different temperatures in a fast kiln (Nannetti), following the firing cycle shown in Fig.

The characterisation of the treated clays and the porcelain stoneware body compositions consisted in being micronised at less than 100 micrometres, so as to be homogeneous enough and to have an accurate grain size that allowed it to be measured correctly by various instrumental techniques, which are detailed in the following. The chemical analysis was performed by an X-ray fluorescence spectrometer (XRF) with a sequential X-ray wavelength dispersion S4 Pioneer, Bruker (Rh anode, 4 kW); the mineralogical study was conducted with an X-ray diffractometer (XRD) Bruker-AXS D4 Endeavor in the range of 10°-80° (2θ) with a step of 0.05°/2s; the thermodifferential analysis was carried out by DTA STA 503 Bahr; plasticity was measured by means of a Pfefferkorn apparatus, based on the principle of impact deformation; elemental analysis of organic and inorganic carbon and total sulphur was performed using a SC144 Leco model; the colorimetric parameters were analysed using a Konica Minolta UV-Visible spectrophotometer (CM-3600) and the colour space CIELab; the flexural strength was
determined by a HOYTOM plasticinometer with a load cell of 5000 N and a force threshold of 16N; in the sintering diagram, the linear shrinkage was evaluated by a Mitutoyo digital calliper, considering the initial length ($L_i$) as the length of the dried piece and the final length ($L_f$) as the length of the fired piece: $\%LS=(L_i-L_f)/L_i \cdot 100$, and water absorption (%WA) was determined according to the Quality of Ceramic Tiles Standard (UNE-EN-ISO 10545-3); the microstructural morphology was studied with a scanning electron microscopy (SEM) model JEOL 7001F fitted with an energy dispersive X-ray analyser (EDX), operating at 15-20kV; and the dilatometric analysis was performed using a 801L Bähr dilatometer.

4. RESULTS AND DISCUSSION

4.1 Characterisation of Spanish clays after being treated

In order to present the original quality of these Spanish clays, Fig. shows the comparison of Fe$_2$O$_3$ (wt%), lightness ($L^*$ measured in fired pieces at 1185ºC) and organic carbon (wt%) between Ukrainian clays (CY-01 and CY-02) and Spanish clays (TE-01, TE-02 and CR-01) in their natural state, without being treated. As can be observed, Ukrainian clays displayed about 10 points more in lightness thanks to their low content in iron oxides, while Spanish clays presented at least almost three times more iron oxides than those from Ukraine. However, the only clay that was completely free of organic matter was CR-01, while this impurity reached the highest value in the case of TE-01.

As regards the reduction in organic matter, Fig. shows the DTA of original TE-01 and some TE-01 samples treated by the FCM, where two main peaks can be observed: one exothermic peak at around 400ºC, corresponding to the combustion of organic matter,
and another endothermic peak representing the dehydroxylation of kaolinite. In this sense, the DTA curve indicates that the combustion peak is reduced while the treatment temperature increases with a residence time of 30 minutes. At the same time, the dehydroxylation peak is reduced in the same direction but with a lower tendency. Two other common peaks of clays also appear in the DTA: at 573°C there is an endothermic peak representing the allotropic transformation alpha-quartz to beta-quartz, and at 960°C there is the exothermic reaction of mullite formation.

Fig. shows the variation of organic matter and kaolinitic dehydroxylation vs temperature, calculated from area measurements of DTA peaks. At 350°C, the organic matter is still excessive and the water of constitution of the kaolinite is almost the same as in the original clay. However, at 400°C there is around 30 wt% of organic matter although the dehydroxylation is similar to the case of 350°C. At 500°C and 600°C, the removal of organic matter increases but dehydroxylation is higher.

The importance of avoiding kaolinitic dehydroxylation is related to the fact that, thanks to its plasticity, the presence of kaolinite allows the clay to be shaped when it is wet—a characteristic of clays. Hence, plasticity, measured using the Pfefferkorn index (Andrade et al., 2011), is inversely proportional to the temperature, as determined in Table 2, because the water of constitution of the kaolinite has disappeared with temperature. With the treatment at 400°C-30 min, the plasticity presents similar values to the original TE-01 and Ukrainian clays: 24 vs 28 Pfefferkorn index. Regarding organic matter, in this case, at 400°C there is a significant reduction from 0.52 to 0.10 wt%, according to the results of the elemental analysis obtained from a LECO device. This reduction is similar to those corresponding to 500°C and 600°C, but these tests present
lower plasticity values. Consequently, it is considered that the optimal result is the treatment of TE-01 at 400°C for 30 minutes.

Table 2. Comparison of Pfefferkorn index of plasticity and organic carbon (wt%) presence between Ukrainian clays and TE-01 (original and treated at 400°C - 30 min).

<table>
<thead>
<tr>
<th>Pfefferkorn index</th>
<th>CLAYS</th>
<th>CY-01</th>
<th>CY-02</th>
<th>Original TE-01</th>
<th>TE-01 350°C-30 min</th>
<th>TE-01 400°C-30 min</th>
<th>TE-01 500°C-30 min</th>
<th>TE-01 600°C-30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic carbon (wt%)</td>
<td>CY-01</td>
<td>CY-02</td>
<td>Original TE-01</td>
<td>TE-01 350°C-30 min</td>
<td>TE-01 400°C-30 min</td>
<td>TE-01 500°C-30 min</td>
<td>TE-01 600°C-30 min</td>
<td></td>
</tr>
<tr>
<td>Pfefferkorn index</td>
<td>29</td>
<td>27</td>
<td>28</td>
<td>26</td>
<td>24</td>
<td>20</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Organic carbon (wt%)</td>
<td>0.08</td>
<td>0.05</td>
<td>0.52</td>
<td>0.48</td>
<td>0.10</td>
<td>0.06</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

The comparative chemical analysis of the original and the treated TE-02 clay is indicated in Table 3. After being treated by the three methods, TE-02, contaminated with iron carbonate or siderite as given in Fig., has reduced the Fe₂O₃ content 60% wt in all cases. This suggests that the siderite is mainly located in the coarse fraction over 100 micrometres and the siderite particles below this mesh are difficult to separate by means of HCM or the EFM. Experience with these types of minerals suggests that this could most probably be caused because siderite particles are confined in quartz granules. Consequently, these granules would be too heavy to be separated by HCM and their magnetic susceptibility is too low to be caught by the EFM.

Table 3. Chemical analysis (wt%) of TE-02 measured by the X-ray fluorescence method (XRF) after being treated.

<table>
<thead>
<tr>
<th>TE-02 (siderite)</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORIGINAL</td>
<td>0.29</td>
<td>0.89</td>
<td>21.09</td>
<td>59.42</td>
<td>3.34</td>
<td>0.32</td>
<td>0.91</td>
<td>5.39</td>
<td>8.51</td>
</tr>
<tr>
<td>100 µm WSM</td>
<td>0.52</td>
<td>0.69</td>
<td>23.21</td>
<td>61.25</td>
<td>3.46</td>
<td>0.24</td>
<td>0.87</td>
<td>2.21</td>
<td>7.32</td>
</tr>
<tr>
<td>HCM</td>
<td>0.54</td>
<td>0.72</td>
<td>23.74</td>
<td>61.34</td>
<td>3.48</td>
<td>0.13</td>
<td>0.62</td>
<td>2.17</td>
<td>7.25</td>
</tr>
</tbody>
</table>
In the case of CR-01 clay, the WSM reduces the amount of Fe$_2$O$_3$ contained in it by around 64 wt%, corresponding to hematite (see Fig.), while the HCM allows a reduction of 72 wt% (Table 4). However, the hematite content is still too high to be used as white clay (Fig.). With the EFM, the hematite content in CR-01 is reduced by around 80 wt%, with respect to the original Fe$_2$O$_3$ content (in wt%). Thus, its iron oxide content is similar to that of Ukrainian clays (CY-01, see Fig.). In this case, both methods, HCM and EFM, are useful to reduce the hematite content (wt%) in CR-01 clay by around 70%, at least. This could be produced thanks to the fact that the hematite particles in CR-01 clay are not confined in granules with other materials, and have a weight that is low enough to be caught by HCM and exhibit an adequate magnetic susceptibility to be extracted by means of EFM.

### Table 4. Chemical analysis (wt%) measured by the X-ray fluorescence method (XRF) of CR-01 after being treated.

<table>
<thead>
<tr>
<th>CR-01 (hematite)</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>TiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORIGINAL</td>
<td>0.82</td>
<td>0.07</td>
<td>23.45</td>
<td>59.77</td>
<td>2.72</td>
<td>0.01</td>
<td>1.14</td>
<td>6.05</td>
<td>5.76</td>
</tr>
<tr>
<td>100 µm WSM</td>
<td>0.80</td>
<td>0.17</td>
<td>26.71</td>
<td>59.50</td>
<td>3.39</td>
<td>0.05</td>
<td>1.15</td>
<td>2.17</td>
<td>5.85</td>
</tr>
<tr>
<td>HCM</td>
<td>0.96</td>
<td>0.22</td>
<td>27.5</td>
<td>58.2</td>
<td>3.19</td>
<td>0.13</td>
<td>1.18</td>
<td>1.64</td>
<td>6.31</td>
</tr>
<tr>
<td>EFM</td>
<td>0.93</td>
<td>0.24</td>
<td>26.91</td>
<td>59.84</td>
<td>2.81</td>
<td>0.09</td>
<td>1.06</td>
<td>1.18</td>
<td>6.52</td>
</tr>
</tbody>
</table>

* Loss on ignition

### 4.2 Characterisation of compositions
The compositions studied here present the expected tendency of chemical analysis, hence composition A, formulated from untreated Spanish clays, contains 1.39 wt% Fe$_2$O$_3$, while composition B, reformulated with the treated clays and after removal of around 60 wt% of siderite and around 80 wt% of hematite impurities, exhibits only 0.86 wt% Fe$_2$O$_3$, which is comparable with the STD composition (Table 5).

Table 5. XRF results corresponding to compositions A, B and STD.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>TiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD</td>
<td>4.31</td>
<td>0.7</td>
<td>19.7</td>
<td>67.5</td>
<td>1.24</td>
<td>0.79</td>
<td>0.59</td>
<td>0.73</td>
<td>3.86</td>
</tr>
<tr>
<td>A</td>
<td>3.94</td>
<td>0.6</td>
<td>19.5</td>
<td>67.7</td>
<td>1.22</td>
<td>0.81</td>
<td>0.77</td>
<td>1.39</td>
<td>4.06</td>
</tr>
<tr>
<td>B</td>
<td>3.89</td>
<td>0.8</td>
<td>19.6</td>
<td>67.8</td>
<td>1.64</td>
<td>0.66</td>
<td>0.63</td>
<td>0.86</td>
<td>3.48</td>
</tr>
</tbody>
</table>

* Loss on ignition

The importance of iron removal is directly related to the visual aspect of the stoneware bodies when they are fired at maximum densification temperatures, which in this case are around 1165ºC and 1185ºC. The colorimetric parameters expressed using the CIELab system of each temperature are shown in Table 6. The parameter $a^*$ ($a^*>0$ red; $a^*<0$ green) increases when the Spanish clays are used without being previously treated in composition A, but if the iron impurities are removed (composition B), this parameter is reduced significantly with a value similar to the composition STD. At the same time, $b^*$ ($b^*>0$ yellow; $b^*<0$ blue) increases with raw Spanish clays, but goes down when the treatment is applied. Finally, the parameter $L^*$ ($L^* = 0$ black; $L^* = 100$ white) decreases with temperature, and is improved if treated clays are used in the formulation of the porcelain stoneware body (Table 6).

Table 6. Colorimetric parameters of compositions A, B and STD for 1165ºC and 1185ºC measured by the CIELab system.

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>T (ºC)</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD</td>
<td>1165</td>
<td>74.76</td>
<td>2.01</td>
<td>11.08</td>
</tr>
<tr>
<td>A</td>
<td>1185</td>
<td>70.67</td>
<td>2.26</td>
<td>12.23</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>64.88</td>
<td>2.71</td>
<td>11.79</td>
</tr>
<tr>
<td>STD</td>
<td></td>
<td>69.19</td>
<td>2.42</td>
<td>12.79</td>
</tr>
</tbody>
</table>
As regards the removal of organic matter, Table 7 summarises the values for compositions related to the presence of this impurity in TE-01 clay. The thermal treatment of this clay allows the amount of organic matter in composition B to be reduced to levels similar to those of composition STD, but the decrease in plasticity due to the dehydroxylation of the clay (a parameter that is essential to allow the stage involving the pressing of ceramic bodies) is not notable. Moreover, the flexural strength of the still-unfired dried pieces is very similar in the three compositions. Consequently, the use of this treated clay in the porcelain compositions is possible.

Table 7. Results of organic carbon measurement (wt%), plasticity measurement (Pfefferkorn index) and flexural strength for dried pieces (N/mm²) of compositions A, B and STD.

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>Organic carbon (wt%)</th>
<th>Pfefferkorn index (wt%)</th>
<th>Flexural strength for dried unfired pieces (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD</td>
<td>0.00</td>
<td>21.23</td>
<td>3.67</td>
</tr>
<tr>
<td>A</td>
<td>0.20</td>
<td>20.86</td>
<td>3.61</td>
</tr>
<tr>
<td>B</td>
<td>0.05</td>
<td>20.35</td>
<td>3.65</td>
</tr>
</tbody>
</table>

Fig. 7 shows the sintering diagram of each composition, namely the linear shrinkage (L.S.) and the water absorption (W.A.) vs temperature according to the industrial firing cycle plotted in Fig. 2. The shrinkages of compositions A and B are very similar to that of STD, while both A and B present lower W.A. values than STD, thereby allowing higher densification at a lower temperature.

The scanning electron micrographs of each composition, measured in pieces fired at 1185°C, can be seen in Fig. 8. It is worth noting the reduction in the size and number of bright areas, corresponding to the heavier elements, these being iron and titanium compounds in the case of composition B, the result being a micrograph similar to that obtained for composition STD. Furthermore, there is no significant difference in the open
porosity, which matches the water absorption obtained from the sintering diagram (Fig. 7).

Finally, the dilatometric results of the compositions under study, expressed as alpha parameters, are comparable enough to be used as porcelain stoneware body or composition STD (Table 8).

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>ALPHA·10^7 1/K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C-300°C</td>
</tr>
<tr>
<td>STD</td>
<td>69.16</td>
</tr>
<tr>
<td>A</td>
<td>68.50</td>
</tr>
<tr>
<td>B</td>
<td>69.72</td>
</tr>
</tbody>
</table>

Table 8. Dilatometric results of compositions STD, A and B.

5. CONCLUSION

Three Spanish clays from the provinces of Teruel and Ciudad Real, containing impurities of iron compounds and organic matter, were treated physically and characterised for use in the formulation of porcelain stoneware body, substituting the clays imported mainly from Ukraine, Germany and United Kingdom. The methods used to remove the iron in two clays were the mechanical stirrer, the hydrocyclone and the electromagnetic filter, obtaining an iron removal rate of 60 wt% (siderite), 72 wt% (hematite) and 80 wt% (hematite), respectively. The thermal treatment allowed the amount of organic matter to be reduced to acceptable levels for use as a white clay, while keeping enough plasticity to allow it to be pressed. All these treated clays have permitted the formulation of a composition of porcelain stoneware body that is very similar to the standard composition, thus improving the properties of these contaminated Spanish clays and saving the need to rely on clays imported from other countries.
Acknowledgements

The authors are grateful to the Spanish Government for the financial support given to this work through the National Research Programmes RETO INVESTIGACIÓN “SUNBEAM” (ENE2013-49136-C4-2-R) and RETO COLABORACIÓN “ECOART” (RTC-2014-2294-3).
References


Parra, J., 1996. Mineralogy and ceramic properties of paleozoic slate rocks from Ciudad Real, Doctoral Thesis, University of Castilla y La Mancha (Spain).


407 List of figures

408 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.

410 Fig. 2. Graph representing the industrial firing cycle used to obtain ceramic porcelain tiles.

412 Fig. 3. Comparison of ball clays with Spanish clays before treatment designed for use in porcelain stoneware formulation.

414 Fig. 4. DTA curves corresponding to TE-01 (original and treated for 30 minutes at different temperatures).

416 Fig. 5. Removed organic matter (wt%) and removed kaolinitic dehydroxylation (wt%) of TE-01 treated at different temperatures for 30 minutes.

418 Fig. 6. X-ray diffractograms of sieve residue obtained at 100 micrometres (R100) corresponding to Spanish clays TE-02 and CR-01. TE-02 R100 and CR-01 R100 are the residues of TE-02 and CR-01 clays sieved at 100 micrometres, respectively.

420 Fig. 7. Sintering diagram: linear shrinkage and water absorption vs temperature of compositions A, B and STD.

422 Fig. 8. Scanning electron micrographs of pieces fired at 1185ºC: a) composition STD, b) composition A, and c) composition B.