Green thinking in the ceramic industry-porcelain stoneware tiles from low-impact raw materials

M. Lassinantti Gualtieri*, D. Settembre Blundo*, A.M. Ferrari*, F. E. Garcia Muñiz*, C. Siligardi

*Gruppo Ceramico GRESMALT SpA

The purpose of this action is the design of a porcelain tile composition containing at least 20-30 wt.% of raw materials delivered by rail instead of by road, leading to a lower environmental impact of the final product. Nowadays, clay raw materials for ceramic production in the Sassuolo district (Italy) are supplied by several different transportation modes including rail, road and water although road transportation is the most common one to limit road transport, at least in Europe, one viable way is to use German clays delivered by train. Currently, porcelain stoneware tile compositions mainly contain high-quality clays from Ukraine and Germany, with limited amounts of clays of lower quality from Spain, Portugal and national territory. To satisfy the market trend, increasingly oriented towards the use of large formats (40x80, 60x120, 120x240cm), the properties of the clay component in the raw materials mixture is very important. In fact, high mechanical strength in the green state becomes crucial in order to avoid mechanical damage during glazing and decoration. From this point of view, the Ukrainian clay is preferred due to its high plasticity. Another important advantage is its high fusibility. Taking all this into account and to pursue the aim of the research, the focus was focused on characterizing the technological properties of German clays transported by rail and including them in novel formulations.

AIMS OF WORK
- Individualize and characterize German clays available on the market
- Formulate novel compositions by partially substituting the Ukrainian clays with German ones

RAW MATERIALS and NOVEL MIXTURES

Table 1: Chemical and mineralogical compositions (wt%) of german (TED) and UK clays used in the study

<table>
<thead>
<tr>
<th>Oxide</th>
<th>UK</th>
<th>TED1</th>
<th>TED2</th>
<th>TED3</th>
<th>TED4</th>
<th>TED5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>58.5</td>
<td>65.8</td>
<td>67.0</td>
<td>65.6</td>
<td>59.8</td>
<td>67.7</td>
</tr>
<tr>
<td>Al2O3</td>
<td>27.5</td>
<td>23.3</td>
<td>21.0</td>
<td>21.0</td>
<td>28.0</td>
<td>10.9</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>1.5</td>
<td>1.2</td>
<td>1.2</td>
<td>2.0</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>TiO2</td>
<td>1.3</td>
<td>1.4</td>
<td>1.2</td>
<td>1.6</td>
<td>2.4</td>
<td>1.5</td>
</tr>
<tr>
<td>MgO</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
<td>0.2</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.6</td>
<td>0.0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>K2O</td>
<td>2.6</td>
<td>1.8</td>
<td>2.1</td>
<td>2.3</td>
<td>1.7</td>
<td>1.9</td>
</tr>
<tr>
<td>LOC</td>
<td>7.2</td>
<td>7.5</td>
<td>6.2</td>
<td>6.3</td>
<td>8.6</td>
<td>6.2</td>
</tr>
</tbody>
</table>

The mineralogical compositions of the German clays are different with respect to that of the Ukrainian clay, the former ones being more kaolinitic and the latter one more ilitic. The Ukrainian clay is more rich in Na2O which acts as flux. This is an important aspect to consider when formulating new mixtures.

Table 3: new mixtures containing #5 TED clay

<table>
<thead>
<tr>
<th>Industrial mix</th>
<th>MT8</th>
<th>K3</th>
<th>FL5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ukraine clay</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>German clay</td>
<td>30</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Turkish Na-feldspar</td>
<td>20</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Italian Nafeldspar</td>
<td>20</td>
<td>/</td>
<td>23</td>
</tr>
<tr>
<td>Italian sand</td>
<td>25</td>
<td>/</td>
<td>7</td>
</tr>
<tr>
<td>Feldspar sand</td>
<td>/</td>
<td>7</td>
<td>25</td>
</tr>
</tbody>
</table>

The preliminary investigations show that the German clays have similar technological properties but are different from the Ukrainian clay (not shown here). Following the same grinding process, the Ukrainian clay is finer (residue 0.8 %) and has higher fluxing action (water absorption 0.02%) and linear firing shrinkage (8.5 %). Also the viscosity measured with the Ford cup is higher, possibly indicating a higher plasticity. These results show that a simple substitution of the Ukrainian clay with German ones is not possible without changing the technological properties. An alternative approach is to completely reformulate the raw materials mixture, by matching the chemistry of the novel formulation with the standard containing the Ukrainian clay, particularly concerning the Na/K ratio. This work is the second part of the action. Table 2 shows the chemical compositions of the raw materials used for the novel formulations, including the German clay nr.5 which was found most suitable.

Table 2: Chemical compositions (wt%) of the raw materials used in the study

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Ukraine clay</th>
<th>German clay</th>
<th>Turkish Na-feldspar</th>
<th>Italian Na-feldspar</th>
<th>Italian sand</th>
<th>Feldspar sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>58.5</td>
<td>67.7</td>
<td>69.5</td>
<td>67.4</td>
<td>67.7</td>
<td>65.8</td>
</tr>
<tr>
<td>Al2O3</td>
<td>27.5</td>
<td>20.4</td>
<td>18.5</td>
<td>12.5</td>
<td>11.5</td>
<td>23.3</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>1.5</td>
<td>1.6</td>
<td>0.2</td>
<td>0.9</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>TiO2</td>
<td>1.3</td>
<td>1.0</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td>1.6</td>
</tr>
<tr>
<td>MgO</td>
<td>0.5</td>
<td>0.4</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.6</td>
<td>0.1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>K2O</td>
<td>2.6</td>
<td>1.9</td>
<td>0.5</td>
<td>0.7</td>
<td>2.6</td>
<td>1.8</td>
</tr>
<tr>
<td>LOC</td>
<td>7.2</td>
<td>6.3</td>
<td>8.6</td>
<td>6.2</td>
<td>7.2</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The results allowed to deeper understand the changes in sintering behavior induced by the introduction of the German clay. The raw materials mixtures were wet ground using standard laboratory equipment (65 wt.% dry material and 35 wt.% water) until a solid residue <5 wt.% was achieved (45 µm sieve). The powder obtained from drying the slip was humidified to 6 wt.% and uniaxially pressed (470 kg/cm²) to obtain cylinders with a diameter of 50 mm. Following firing in an industrial kiln, some technological properties were determined as shown in Table 4.

Table 4: technological parameters of the studied mixtures (Buller 1100°C)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>W.A.</th>
<th>Linear shrinkage (%)</th>
<th>Linear thermal expansion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT8</td>
<td>1.73</td>
<td>5.7</td>
<td>-0.3</td>
</tr>
<tr>
<td>K3</td>
<td>0.35</td>
<td>5.0</td>
<td>0.9</td>
</tr>
<tr>
<td>FL5</td>
<td>0.43</td>
<td>6.6</td>
<td>0.0</td>
</tr>
</tbody>
</table>

RESULTS

The preliminary results presented here show that the sintering behavior of the mixture containing 20 wt.% of German clay (K3) is similar to that observed for the standard industrial mixture. In fact, the technological parameters differ less than 10% from the standard. Instead, the water absorption and the linear firing shrinkage of MTB and FL5, respectively, are too high. We can thus conclude that the composition K3 best satisfies the purpose of this action, being the design of a porcelain stoneware tile formulation containing at least 20 wt.% of raw materials transported on rail.

CONCLUSIONS

Acknowledgements
The authors would like to thank European Union for financial funding and POOL-ITI for the administrative support.