CHARACTERIZATION AND POTENTIAL APPLICATION OF PLIOCENE CLAYS FROM MENZEL TEMIME REGION (NORTHEAST OF TUNISIA) FOR BRICK AND FAIENCE CERAMICS FABRICATION

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ABSTRACT
The Pliocene in Menzel Temime region (Northeast of Tunisia) overlying the Saouaf formation of Middle Miocene age, is represented by three lithostratigraphic formations: Potter clays, sand of Nabeul and Sidi Barka clays. Clay fractions consist of kaolinite and illite with plastic properties and minor quartz, calcite and feldspar. Applications of clays in bricks and faience ceramics are reported. However, the resulting faience ceramics exhibit some textural defects. These defects could be eliminated by increasing of pressure of the mold.

KEYWORDS: clay, valorization, Pliocene, ceramic, Tunisia

1. INTRODUCTION
Potential source of clay materials for ceramic industry was discovered in the region of Menzel Temime (northeastern Tunisia) (Fig. 1). The stratigraphic sequence overlying the Saouaf formation (Middle Miocene) includes three lithostratigraphical formations (Colleuil, 1976), namely Potter clays, sand of Nabeul and Sidi Barka clays (Fig. 2). In the presented study, a detail characterization of these clays is reported including their possible application in brick and faience ceramics production.

2. MATERIALS AND METHODS
Two mixtures of clays were prepared from Potter clays (M1) or from the Sidi Barka clays (M2) with sand of Sidi Aïch (central Tunisia) mixing 80 % of clay with 20 % of sand. The prepared mixtures were dried at 110 °C for 24 hours, then crushed, and mixed with an appropriate quantity of water. Obtained bricks were firstly dried in the oven at 110 °C, afterwards heated at 800, 850, 900 and 950 °C for 1 hour with a thermal cycle of about 4 hours. The temperatures were chosen in line with ceramic industry conditions.

Concerning a ceramic faience production, the mixtures of clays M1S (M1 + 20% of sand) and M2S (M2 + 20% of sand) were after drying in oven at 110°C during 24 hours ground to fine powder. The fine powder was humidified, homogenized and pressed in raw ceramic faiences. The latter were dried in oven at 110°C and heated to 850, 900, 950 and 1000 °C.

Mineralogical analyses were performed by X-ray diffraction (XRD) analysis using Philips diffractometer. Quantification of different phases was carried out by the classic method of diffraction peak area measurement and reflection power (Schultz, 1964; Biscaye, 1965; Barahona, 1974). The chemical analysis was determined by X-ray fluorescence spectrometer. The evaluation of plasticity was performed by Atterberg limits method (L.C.P.C., 1987). “Bigot curve” or “drying curve” was recorded by a barlattograph. Thermogravimetry (TG) and Differential Thermal Analysis (DTA) curves were recorded by simultaneous DTA/TG instrument. Thermal Dilatometric Analysis was carried out by ADAMEL LHOMARGY dilatometer type DM 15 reaching maximum temperature 1000 °C with a heating rate 10 °C/min.

The unfired bricks and faience ceramics were characterized by drying shrinkage \(100\cdot (l_0 - l_s) \cdot l_0^{-1}\), considering \(l_0\) as the length between two features of 20 mm and \(l_s\) the length between two features of 20 mm after drying. Meanwhile, the resulting fired products were characterized by firing shrinkage \(100\cdot (L_s - L_e) \cdot L_e^{-1}\), losses on ignition (LOI) \(100\cdot (m_s - m_e) \cdot m_e^{-1}\) and water adsorption...
The chemical compositions of the studied clay mixtures (Table 2) have proved high iron (Fe₂O₃) contents, about 9.39 % for M₁ or 8.43 % for M₂, respectively, and relatively high K₂O contents for both clay mixtures, being 2.85 % or 2.74 % respectively. Higher iron as well as potassium contents may be attributed to the presence of illitic phase. Further, very low CaO contents correspond to no calcareous clays presented. Plasticity data placed Potter and Sidi Barka clays in the zone of very plastic clays of Casagrande diagram (Fig. 3), with a drying shrinkage 7.97 % for M₁ and 8.7 % for M₂ (Chaâri, 2003). To reduce the value of the drying shrinkage at least to 6 %, to make these clay mixtures suitable for the ceramic industry, the addition of grease-remover containing silica (quartz, sand, sandstone) is necessary. As the optimum value 20 % of sand was added to each clay mixture so that M₁S = M₁ +20 % of sand or M₂S = M₂ +20 % of sand (Fig. 4).

The TG curves indicated a total weight loss of 7 % for M₁ clay mixture and 8 % for M₂ clay mixture, where the DTA curves exhibited three endothermic peaks (Fig. 5). The first one is associated with the loss of adsorbed water, in the range of 25 °C - 200 °C (Baran et al., 2001). The second peak is related to dehydroxylation of clays and occurred between 500 °C and 600 °C, while their complete destruction is noted at higher temperatures, above 880 °C. An exothermic peak at 924 °C indicated the crystal-
The thermal dilatometric curves of both mixtures show the same features (Fig. 6) with an initial dilation followed by a low shrinkage, related to the dehydration of clay components in the temperature range of 25 to 200 °C. The curve shows a progressive increase above 200 °C with a rapid and sharp effect from 570 °C for M1 mixture or 575 °C for M2 mixture respectively, corresponding to $\alpha \rightarrow \beta$ quartz transition (Jouenne, 1990). Above these temperatures, an initially progressive shrinkage was noted indicating the appearance of the vitreous phase. During the cooling, there is $\beta \rightarrow \alpha$ quartz transition. Jordan et al. (2001) reported a decomposition of CaCO$_3$ to CaO at 800 °C but due to negligible amount of CaCO$_3$ in our materials, it was difficult to detect such phenomena.

When the next portion of sand was added to each mixture, the curves of M1S and M2S mixtures showed a reduction in firing shrinkage and an increase in dilation at 600 °C corresponding to $\alpha \rightarrow \beta$ quartz transition. The data are shown in Tables 3 and 4.

M1S and M2S mixtures exhibited relatively high drying shrinkage of 8.2 % or 8.51 %, respectively (Chaâri, 2003), which depends on the amount of water added during the preparation. On the other hand the firing shrinkage is very low with values varying from 1.21 % to 1.56 % for M1S and from 1.3 % to 1.63 % for M2S, compared to those reported by Dondi et al. (1999). The addition of sand to our mixtures is supposed to be the reason of firing shrinkage decline. The data of water absorption (<15 %) and losses on ignition indicate that the prepared mixtures are suitable to produce good quality products. There was a color changing visible during firing process on the bricks (Fig. 7), related to the presence of iron oxides.

Obtained data have indicated that both mixtures of clays had almost the same properties in drying.
Fig. 3  Variation of the plasticity index according to the liquid limit for two mixtures of clays

Fig. 4  Bigot curves of different mixtures
**Table 3** Results of the physical parameters according to the temperature of two mixtures M1S (Potter clays formation +20% of sand) and M2S (Sidi Barka clays formation +20% of sand) (Bricks)

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Drying shrinkage (%)</th>
<th>Temperature (°C)</th>
<th>Firing shrinkage (%)</th>
<th>LOI (%)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1S</td>
<td>8.2</td>
<td>800</td>
<td>1.21</td>
<td>7.31</td>
<td>14.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>1.34</td>
<td>7.015</td>
<td>14.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>1.51</td>
<td>6.52</td>
<td>13.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>1.56</td>
<td>6.87</td>
<td>13.33</td>
</tr>
<tr>
<td>M2S</td>
<td>8.51</td>
<td>800</td>
<td>1.3</td>
<td>8.35</td>
<td>14.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>1.42</td>
<td>8.93</td>
<td>11.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>1.58</td>
<td>8.49</td>
<td>11.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>1.63</td>
<td>8.74</td>
<td>9.40</td>
</tr>
</tbody>
</table>

Fig. 5 DTA-TG curves of M₁ and M₂ mixtures
Fig. 6  Dilatometric curves of mixtures

Table 4  Results of the physical parameters according to the temperature of two mixtures M₁S (Potter clays formation +20 % of sand) and M₂S (Sidi Barka clays formation +20 % of sand) (Ceramic faïences)

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Drying shrinkage (%)</th>
<th>Temperature °C</th>
<th>Firing shrinkage (%)</th>
<th>LOI (%)</th>
<th>Porosity (%)</th>
<th>Mechanical resistance to the inflection (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁S</td>
<td>0.9</td>
<td>850</td>
<td>1.3</td>
<td>6.8</td>
<td>13.5</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>0.48</td>
<td>6.9</td>
<td>13.40</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>1.55</td>
<td>7.2</td>
<td>12.1</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>1.7</td>
<td>7.23</td>
<td>11.52</td>
<td>3.6</td>
</tr>
<tr>
<td>M₂S</td>
<td>1.3</td>
<td>850</td>
<td>1.5</td>
<td>7.96</td>
<td>13.52</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>1.62</td>
<td>8.17</td>
<td>12.95</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>1.65</td>
<td>8.88</td>
<td>11.8</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>1.75</td>
<td>9.03</td>
<td>9.5</td>
<td>4.19</td>
</tr>
</tbody>
</table>
shrinkage, firing shrinkage, water absorption, losses on ignition and mechanical resistance to the flexion excluding the latter favorable to be used for faience ceramics. Mechanical resistance to the flexion varies with average value 4.62 N/mm² for M₁₅ and 3.31 N/mm² for M₅₀. The textural examination of produced faience ceramics revealed some defects in final products such as warping or small cracks on the surface (Fig. 8). Such defects appear to be related to the quality of the loading mold, which caused a weak mechanical resistance to the flexion. An increase of the pressure of the mold would reduce significantly such defects and improve the quality of the final products (Jridi, 1986).

4. CONCLUSION

The clays of Pliocene from Menzel Temime region (Northeast of Tunisia) may be classified as “illitic-kaolinitic clays” with low contents of CaCO₃ for less calcareous character. Therefore they could be considered as favorable potential candidates for bricks and faience ceramics production. The addition of 20% of sand to the original raw clay is supposed to be crucial, notably improving the quality of the bricks. In case of faience ceramics, the obtained products revealed some textural defects as warping, small cracks on the surface. These defects appear to be related to the bad loading of the mold. Further tests have to be conducted to improve the quality of the obtained products to come closely to the industry operating conditions.

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Fig. 7 Bricks manufactured from two mixtures of clays $M_{1S}$ and $M_{2S}$

Fig. 8 Ceramic faïences manufactured from $M_{2S}$ mixture