

ASSESSMENT OF THE CERAMIC SUITABILITY OF A RAW CLAY

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Ceramic suitability of an illitic-chloritic raw clay is assessed by means of empirical diagrams, involving grain size distribution, mineralogy, chemical composition and Atterberg limits, and by adopting a new approach basing on the methodology of the experimental design. For the later purpose, the simultaneous effects of the firing cycle parameters (temperature, soaking time and heating rate) on some ceramic properties were evaluated and taken into consideration. The use of the empirical diagrams showed that the studied clay was particularly suitable for pottery and amendments were required for manufacturing structural bodies or red stoneware tiles. By using the statistical method, it was found that the raw material was rather suitable for preparing different kinds of ceramic products, which their appropriate firing parameters could be predictable. These results were discussed in the sight of the microstructural investigations.

INTRODUCTION

Ceramic suitability of clays depends mainly on their characteristics such as mineralogy, chemistry, granulometry and plasticity as well as the firing conditions: temperature, soaking time, heating rate and atmosphere. To assess a clay suitability for manufacturing bricks or roofing, floor and wall tiles empirical diagrams involving grain size distribution [1], mineralogical constitution [2-7] and chemical composition [8-10] are often in use.

Taking for instance the evaluation of the ceramic suitability of raw clay by using the Winkler's diagram [1], no attention is paid to their mineralogical and chemical compositions as well as to firing conditions. This is partly applicable for the remaining known diagrams. In all cases, by using the empirical methods, the technological magnitudes of the foreseeable clay products could not be known.

The aim of this study was to assess the ceramic suitability of an illitic- chloritic raw clay by using empirical diagrams and a new approach involving the methodology of the experimental design.

MATERIALS AND METHODS

The studied argillaceous material was from the east side of the high atlas mountain (morocco) [11]. It consisted of micaceous species, chlorite, quartz, hematite and serpentine (40, 15, 22, 8 and 5 wt.% re-

spectively). The balance was comprised K-feldspar, carbonate and sulfate. The clay chemical composition is given in Table 1.

Table 1. Chemical composition (wt.%) of the studied raw clay.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	^a LOI
50.8	19.2	9.4	4.3	0.3	1.6	4.3	0.8	0.05	8.3

^a Loss On Ignition

The clay grain size fractions (<2 μm and >20 μm), required for the Winkler's diagram, were isolated by sedimentation according to the law of Stokes. The liquidity and plasticity limits (LL, PL) of the clay were conventionally determined, when the index of plasticity (IP) was deduced using the relation $IP = LL - LP$.

The water absorption of samples fired at $800 \leq T \leq 1050$ °C in open atmosphere was assessed by weighting shards before and after immersion in boiled water for 2 hours. The standard deviation was < 0.3 wt. %.

The mathematical equation expressing the relationship between water absorption and temperature, soaking time and heating rate was established by means of the methodology of the experimental design as detailed elsewhere [12].

The microstructure of fired samples was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD analyses were performed on gently grounded samples by a PHILIPS X'Pert MPD X-ray diffractometer, operating with a copper anticathode

($K\alpha = 1.5418 \text{ \AA}$). SEM examinations were realized by a JEOL JMS 5500 scanning electron microscope (SEM) apparatus, equipped with a Falcon EDAX system. For the later purpose, freshly fractured pieces of fired samples were coated with carbon.

RESULTS AND DISCUSSION

Appraisal of the clay ceramic suitability using empirical diagrams

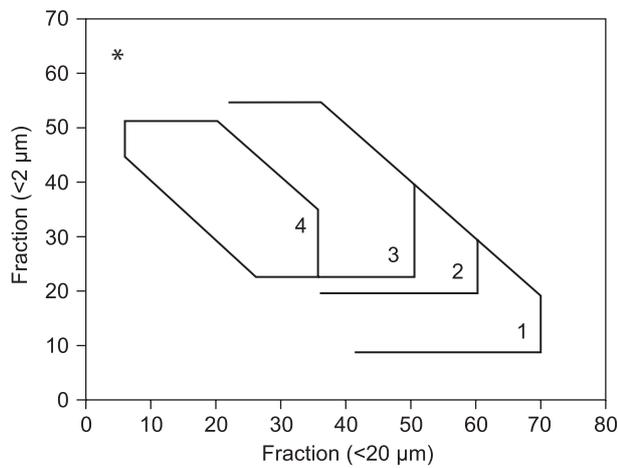
Referring to the point location representing the clay grain size fractions in the Winkler's diagram (Figure 1a), the studied raw material is neither suitable for manufacturing bricks nor roofing tiles. This result is cor-

roborated by the depiction of Figure 1b, where the actual and the appropriate mixtures of phyllosilicates, carbonates and (quartz + feldspars) for roofing tiles and structural clay bodies are presented.

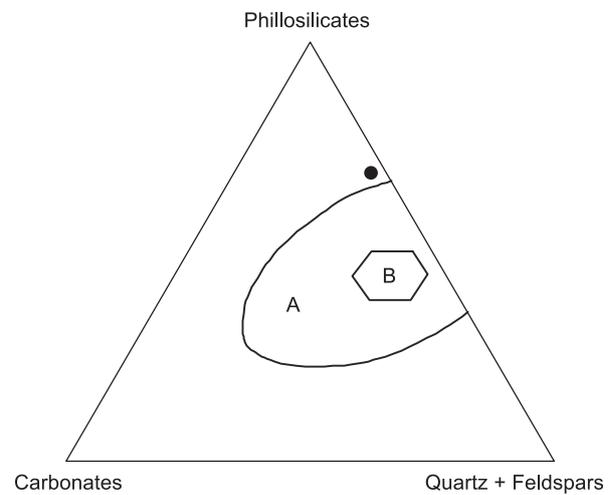
Because of its high amount of fine fraction (62 wt.%), this clay is rather convenient for pottery. This could be supported by the position of the clay Atterberg limits in the diagram of Figure 1c.

In view of these results, the manufacturing of structural products or roofing tiles required for instance additions of coarse grains of tectosilicates and/or carbonates.

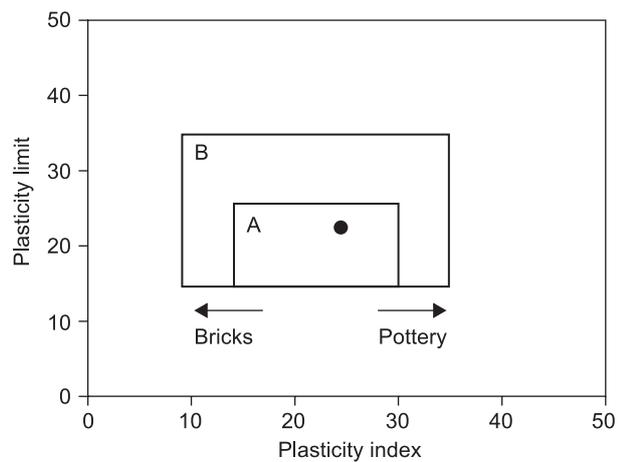
Taking account of the clay chemical composition and the discernible domains of Figure 1d, the considered clay may be used as a feeding material for porous red tiles.



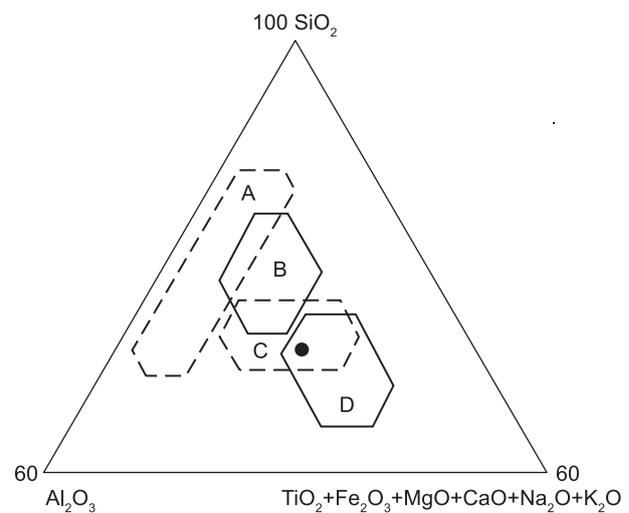
a) Diagram of Winkler [1] presenting the suitable mixtures of grain fractions for manufacturing common bricks (1), vertically perforated bricks (2), roofing tiles and light blocks (3) and thin-walled hollow bricks and blocks (4)



b) Fields of suitable clay compositions for manufacturing structural clay bodies (A) [2-6] and clay roofing tiles (B) [7]

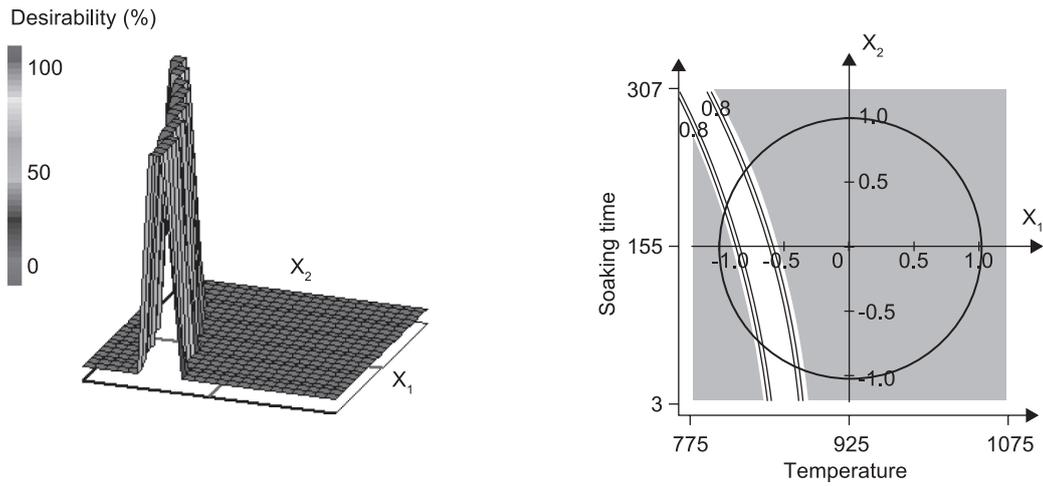


c) Diagram of Bain and Highley [14] showing the optimum (A) and acceptable (B); domains for clay shaping by extrusion

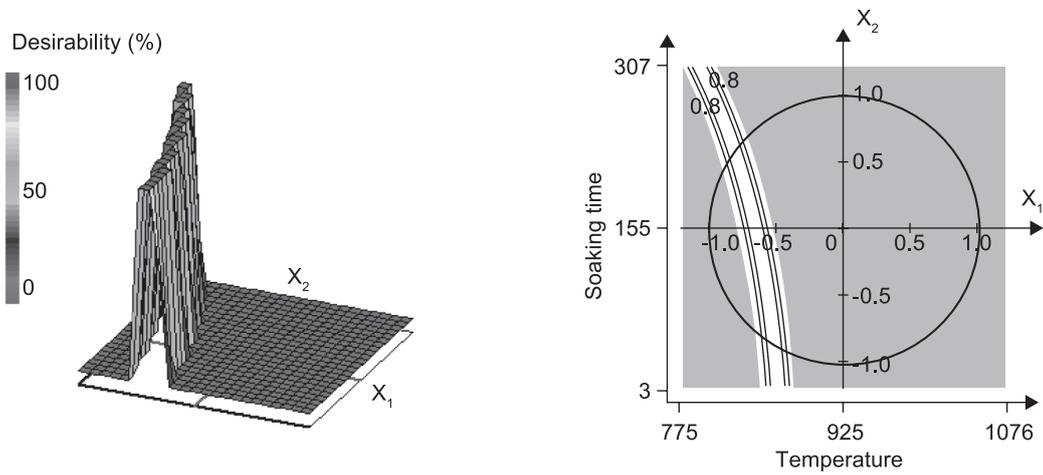


d) Clay chemical composition domains for preparing stoneware tiles (white (A) and red (B) bodies) and porous tiles (C and D) [8-10]

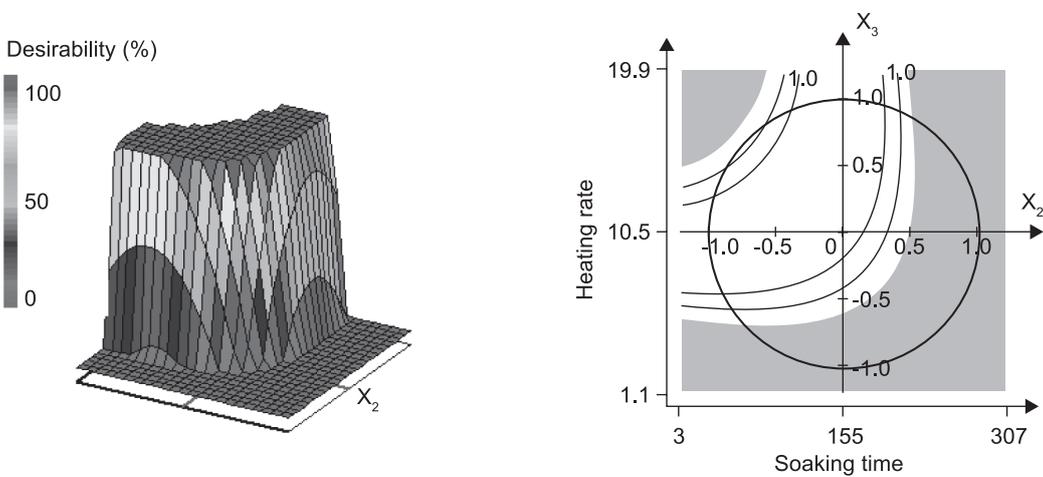
Figure 1. Empirical diagrams showing fields of ceramic bodies which could be prepared from feeding clayey materials.



a) Floor/wall tiles (heating rate = 17°C/min)



b) Roofing tiles (heating rate = 13.2°C/min)



c) Floor/wall tiles (temperature = 834°C)

Figure 2. Desirability domains refer to porous tiles.

Evaluation of the clay ceramic suitability using the statistical method

The use of the methodology of the experimental design showed that the change of water absorption (WA) against firing temperature (T), soaking time (t) and heating rate (h), obeys the equation [12]:

$$WA (\%) = 6.243 - 11.775X_1 - 1.444X_2 + 0.587X_3 + 6.289X_1^2 - 1.29X_2^2 - 1.228X_3^2 + 3.397X_1X_2 - 3.278X_1X_3 - 3.430X_2X_3 \dots \quad (1)$$

where X_1 , X_2 and X_3 are dimensionless parameters, labeled coded variables. They are related to T ($^{\circ}\text{C}$), t (min) and h ($^{\circ}\text{C}/\text{min}$) respectively [$X_1 = (T - 925)/125$; $X_2 = (t - 155)/145$; $X_3 = (h - 10.5)/9.5$].

A comparative evaluation of the algebraic values of the linear terms allows to deduce that T is the most influencing parameter and its increase should lead to

the reduction of water absorption. In fact, it is observed elsewhere that the melt content increased with the rise of temperature and corollary the open porosity was reduced [13].

Regarding the effects of the mutual interactions between the considered firing parameters, it might be retained that T and t interacts in a synergetic way, i.e. the increase of T or t had the same impact on the change of water absorption. However, antagonistic interactions manifested between h and the other remaining parameters.

Porous tiles and bricks manufacturing

Porous tiles can be successfully manufactured by adopting different firing cycles, which can be selected from the desirability domains, i.e. the acceptable values for water absorption, shown as white bands in Figure 2.

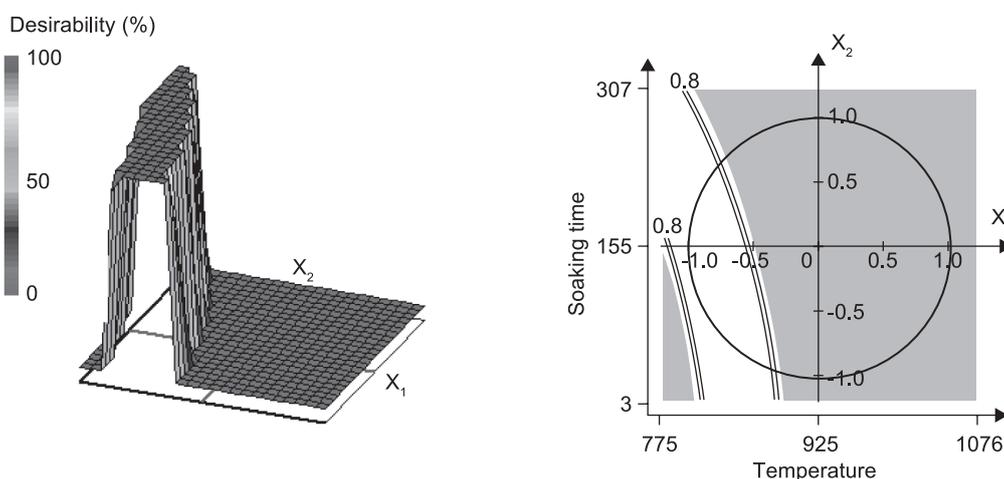


Figure 3. Desirability domains relevant to bricks (heating rate = $16.9^{\circ}\text{C}/\text{min}$).

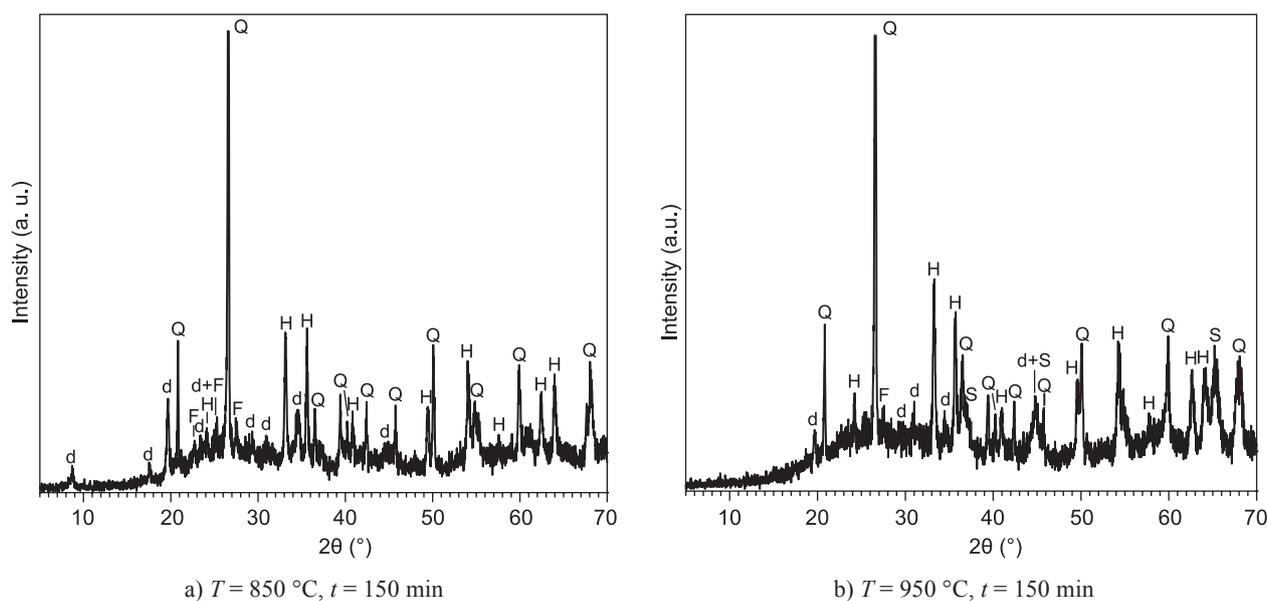


Figure 4. XRD patterns of fired samples. d: dehydroxylated micaceous species ; H : hematite ; F: K-feldspar ; S: spinel ; Q: quartz

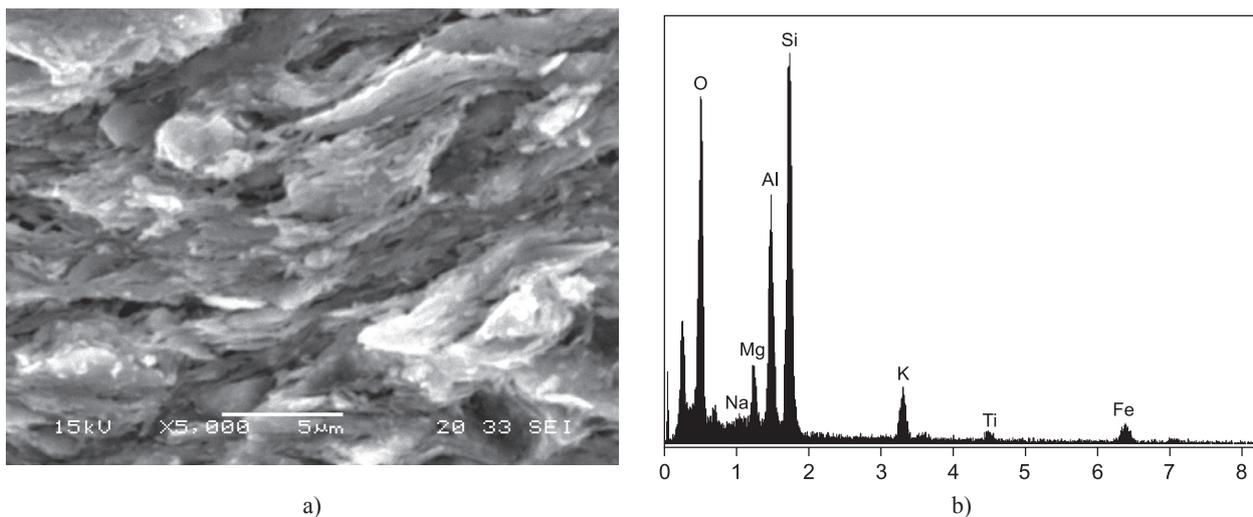


Figure 5. SEM micrograph of a sample fired at 850 °C for 150 min (a). EDS spectrum of dehydroxylated micaceous species (b).

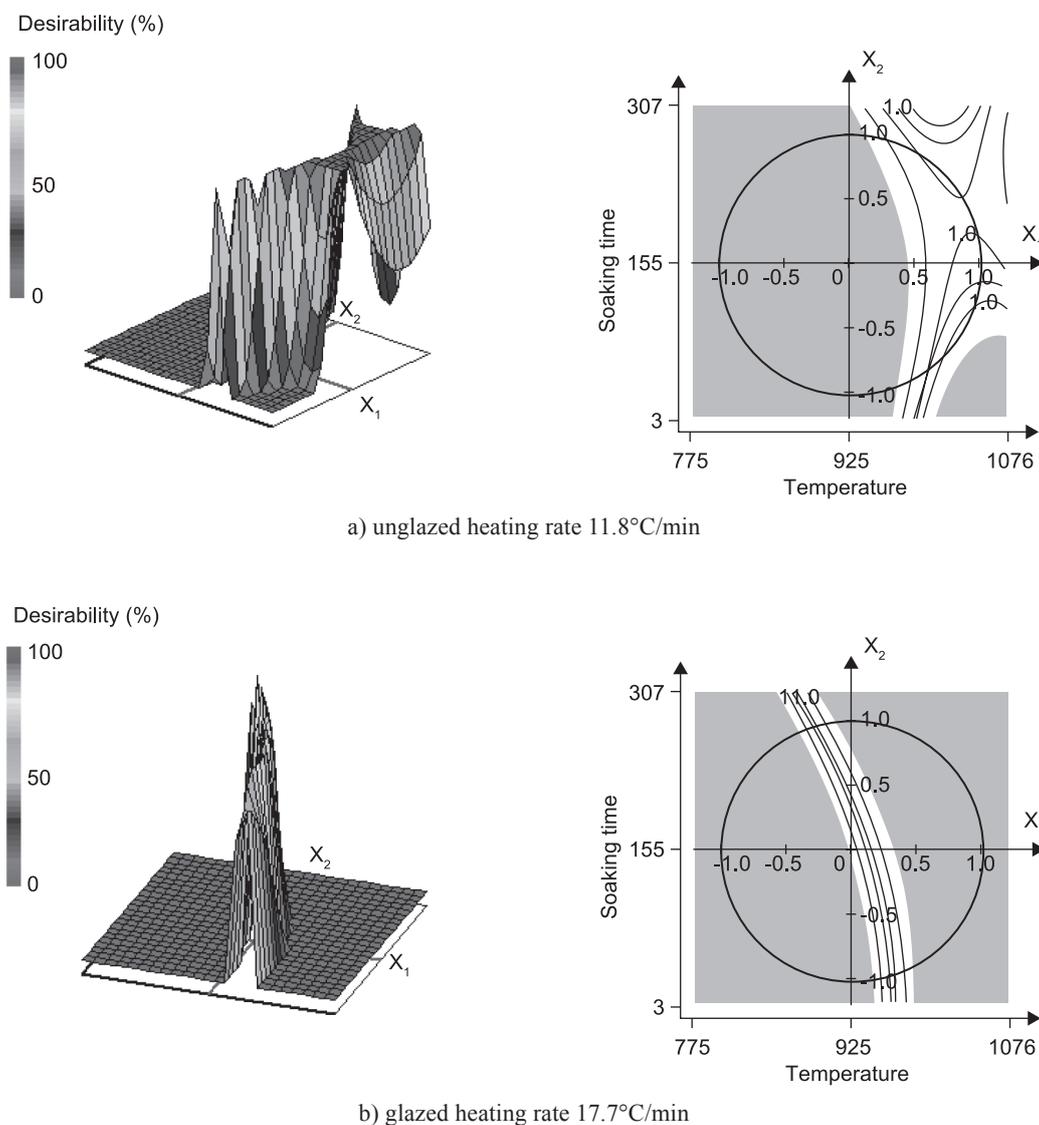


Figure 6. Desirability fields for red stoneware tiles.

However, the appropriate range of firing temperatures is narrow as compared with that of soaking time or heating rate. For bricks manufacturing, it is derived that a less constraint is imposed for selecting soaking time and heating rate, but the suitable firing temperatures should

be in the interval 800- 850 °C (Figure 3). Under such firing conditions, the neoformation process did not take place. However, it was observed that the structure of chlorite and serpentine collapsed and micaceous species transformed to dehydroxylated mica/illite (Figure 4a). As shown in Figure 5, the matrix was essentially composed of dense interconnected filaments, identified as dehydroxylated mica/illite, as well as elongated and abundant pores. Otherwise, the sintering process was not yet significant and the ceramic properties seemed to be mainly controlled by the reorganization and compaction of dehydroxylated clay minerals.

Red stoneware tiles production

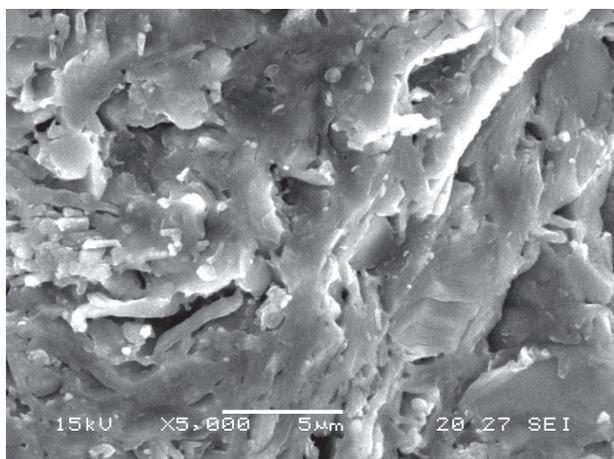
Basing on the plot of Figure 6a, unglazed red stoneware tiles can be prepared by adopting different firing cycles. The suitable temperatures are relatively high as compared to those required for the above porous products. For glazed bodies (Figure 6b), the appropriate temperatures are relatively low, but the temperature interval does not exceed 30°C.

The XRD examinations of samples fired in the acceptable range of temperature to manufacture these products showed the presence of a Mg-spinel phase together with quartz and hematite (Figure 4b). The SEM investigations exhibited a marked reduction of dehydroxylated micaceous filaments and the occurrence of featureless zones which corresponded to the glassy phase (Figure 7a,b). However, because of their small size, the spinel particles could not be evidenced.

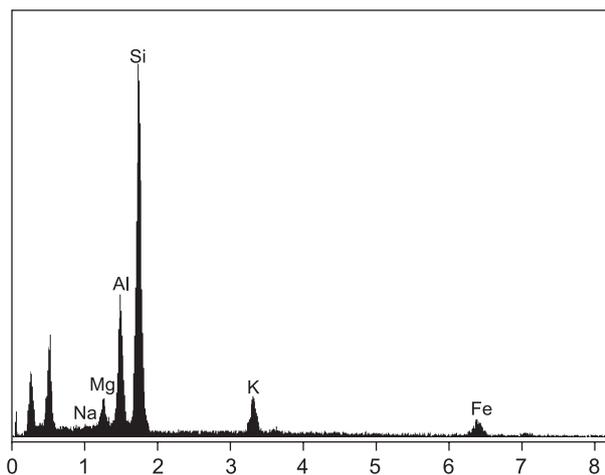
The formation of the liquid phase observed for $T < 950\text{ °C}$ was accompanied with a reduction of the elongated pores. As a consequence, water absorption was reduced, and glazed red stoneware tiles can be successfully manufactured. As the firing temperature increased, quasi-rounded pores formed likely because of the reduction of melt viscosity, and an intense vitrification was observed (Figure 7c) due to quartz melting and the reactivity of dehydroxylated micaceous species. In this case, unglazed red stoneware tiles can be produced. In view of these results, it may be concluded that the manufacture of these products is mainly controlled by the glassy phase formation.

Ceramic manufacturing by using typical slow and fast firing cycles

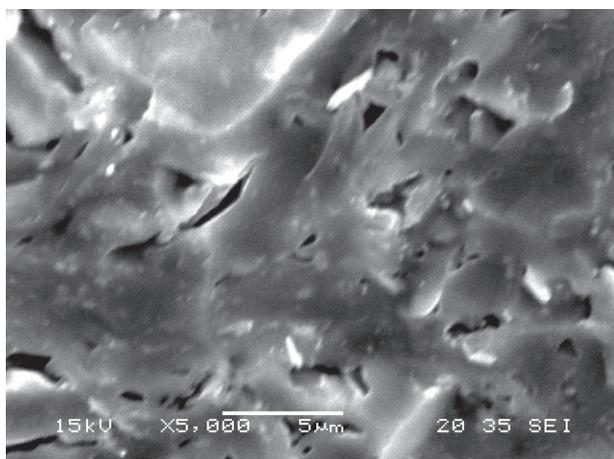
A particular attention is paid to the firing temperature because of its major influence on ceramic properties. The appropriate temperatures for manufacturing different kinds of ceramic products by adopting typical slow ($h = 3\text{ °C/min}$; $t = 280\text{ min}$) and fast ($h = 18\text{ °C/min}$; $t = 30\text{ min}$) firing cycles were evaluated from the curves of Figure 8, which represent the plots of equations (1), (2) and (3). The two latter equations correspond



a) $T = 950\text{ °C}$, $t = 150\text{ min}$



b) Spectrum of the glassy phase



c) $T = 1000\text{ °C}$, $t = 60\text{ min}$

Figure 7. SEM micrographs fired samples and EDS spectrum of glassy phase.

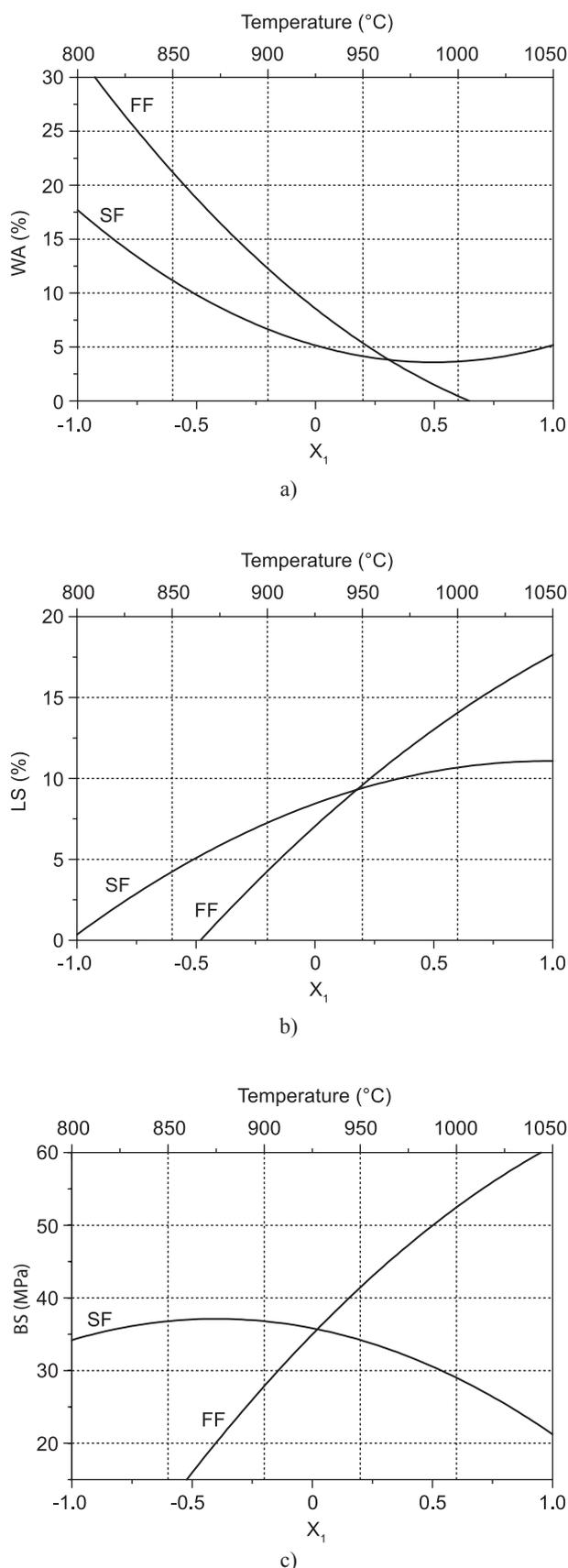


Figure 8. Changes of water absorption (a), linear shrinkage (b) and bending strength (c) versus firing temperature. SF: slow firing; FF: fast firing.

to the variations of the bending strength (BS) and linear shrinkage (LS) against the coded variables. The validation of these equations, which also were obtained by adopting the methodology of the experimental design, is discussed elsewhere [12].

$$BS \text{ (MPa)} = 32.202 + 13.773X_1 + 1.624X_2 + 1.234X_3 - 8.111X_1^2 + 8.343X_2^2 + 7.447X_3^2 - 8.291X_1X_2 + 16.603X_1X_3 + 11.229X_2X_3 \dots \quad (2)$$

$$LS \text{ (%) } = 8.022 + 5.796X_1 + 0.487X_2 - 0.355X_3 - 2.726X_1^2 + 0.012X_2^2 + 0.289X_3^2 - 0.497X_1X_2 + 0.009X_1X_3 + 0.696X_2X_3 \dots \quad (3)$$

By referring to the data of Table 2 and taking account of the plots of Figure 8, it may be deduced that bricks can be successfully manufactured by the adopted slow firing using temperatures laying in the range 800-820°C. For the production of roofing tiles, the domain of firing temperatures is much limited (800-810°C). As concerns red stoneware tiles, they could be prepared by fast firing at around 950°C.

Table 2. Magnitudes of the main technological properties of some clay products [15, 16].

Ceramic products	Bending strength (MPa)	Water absorption (%)	Linear shrinkage (%)
Majolica	15-25	16-24	< 0.5
Monoporosa	20-30	12-18	0-1
Red stoneware tiles	26-43	0-6	5-10
Brick	6-20	15-32	0-2
Roofing tiles	12-22	15-20	0-1

CONCLUSION

The use of the response surface methodology for assessing the ceramic suitability of the illitic-chloritic raw clay was proven to be an effective tool for predicting the manufacture of ceramic bodies, which their eventual production, according to the known empirical diagrams, could not be realized without clay amendments. In addition, its use allowed to evaluate the quantitative effect of each firing cycle parameter on the technological properties of the common clay products.

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