

Characteristics of triassic clays and properties of building ceramics

H. Baccour Zghal^{a,*}, M. Medhioub^b and T. Mhiri^a

^aLaboratoire de l'Etat Solide, Facult des Sciences de Sfax 3018, Sfax-Tunisie.

^bLaboratoire Géoressources, Facult des Sciences de Sfax 3018, Sfax-Tunisie.

This study deals with the mineralogical and thermal analysis of Triassic clays in the south-Eastern Tunisia in order to use them in a faience glazed ceramic. Clays were first analysed by X-ray diffraction, chemical composition, thermal analysis and plasticity. The data collected from these techniques show that illite and kaolinite are the major clay phases. The accessory minerals detected in the powdered rock are; quartz, dolomite and hematite. This study reveals that the amount of silica is relatively high and a plasticity test shows a medium value.

Geotechnical characterization was carried out on the three representative mixtures of Triassic clay samples. Samples were pressed in a rectangular mould and sintered to a temperature ranging from 850 to 1150 °C. Firing characteristics (shrinkage, water absorption, and mechanical resistance to inflection) were measured. Mechanical properties characterizations were performed by means of three-point bending tests. The optimum firing temperature of each sample has been established. The maximum bending strength of each ceramic body has been determined. Porosity-strength relations have been established. These clays could be used in the manufacture of ceramic pieces.

Key words: Clay, Kaolinite, Ceramic, Thermal analysis, Firing.

Introduction

Clay deposit areas have a high economic potential, and soil mineralogical composition, plasticity and porosity are fundamental properties for industrial applications. A faience ceramic is commonly produced from a mixture of raw materials containing a clay, flux and refractory filler [1]. The raw materials used for production of faience mainly consist of quartz and clay minerals.

A potential source of clay materials for the ceramic industry was discovered in Southeastern Tunisia, there is no previous study about these non exploited clay deposits in the region and it is the first time that the applicability of these clays as raw materials for the ceramic industry has been tested.

The main objective of this paper is a study of the chemical-mineralogical compositions and technological behaviour that allows an evaluation of the possibility of the clay deposits studied.

During heating three types of process take place: decomposition, phase transformation, and sintering with partial melting. Both decomposition and phase transformations affect development and extent of the subsequent sintering.

The firing temperature is an important factor enhancing the mechanical resistance and durability of

end products in a faience ceramic, as the material becomes denser. This is also an important engineering quality index for building materials. This effect is due to the progressive formation of calcium silicates and melted phases filling porosity [2], in addition to the high fines content of the raw materials ensuring good compaction during moulding. Both have a positive influence on the mechanical resistance of unfired as well as fired specimen. It has been reported that the presence of calcium carbonate modifies the reactions and affects the formation of the liquid phase [3]. During preheating, the CaCO₃ decomposes to CaO accompanied by the evolution of CO₂ outside the structure of fired bodies between 800 °C and 900 °C. Subsequently, free CaO reacts with amorphosized metakaolinite, which quickly diminishes at an increasing firing temperature [4].

The relationship between water absorption, shrinkage and resistance to inflection as a function of the firing temperature is examined in order to enhance the quality of final products and to optimize the production process.

Materials and methods

Sample material

Three deposits of Triassic clays which can be used in the formulation of ceramic pastes were selected M1, M2 and M3 (Fig. 1). Samples of each clay deposit were collected. In order to ensure a representative sample of each deposit, no less than 50 kg of clay was collected. After extraction, the clay was initially dried

*Corresponding author:
Tel : +21620264354
Fax: +21674274437
E-mail: hajerbaccour@yahoo.fr

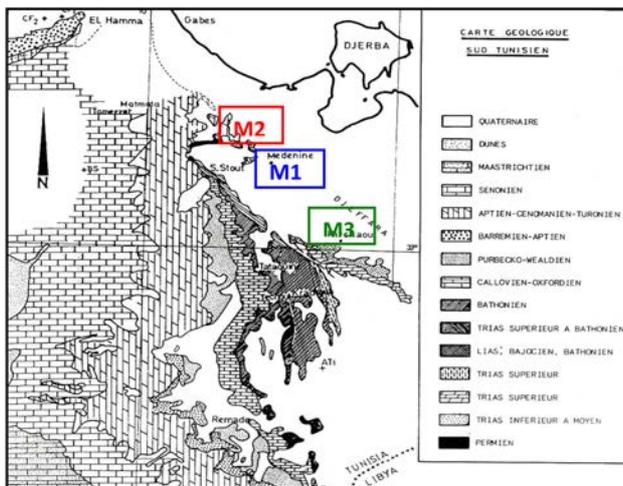


Fig. 1. Location and geological map of three mixtures Triassic clays deposits.

at 110 °C for 24 hours, and then was manually crushed gently to minimize structural damage to the crystal lattice.

The fraction $< 2 \mu\text{m}$ was analysed on glass slides, according to Moore and Reynolds 1989 [5]: The fraction $< 2 \mu\text{m}$ clay was obtained by centrifuging for 10 minutes; in addition, each sample was dispersed in distilled water, ultrasonicated to enhance dispersion, and the $< 2 \mu\text{m}$ fraction collected by settings; a small amount of the clay-water suspension was placed by a pipette onto a slightly ground glass slide and left to dry in order to prepare oriented specimens. For clay mineralogical analysis, samples of these were dried at room temperature, others were glycolated for one hour and solvated to detect expandable minerals, and others heated for three hours at 550 °C to differentiate chlorite and kaolinite. These processes are similar to those described by Thorez [6] and Holtzapffel [7].

X- ray diffraction analysis

The mineralogical analyses of samples were carried out by X-ray diffraction techniques (XRD). The XRD patterns were obtained with an X'Pert Pro PANalytical diffractometer operating at 45 kV and 40 mA, using $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1,5406 \text{ \AA}$). Diffraction patterns were recorded between $3\text{-}60^\circ 2\theta$ at a step size of $0.017^\circ 2\theta$. Quantification of different phases was carried out using the computer program X'pert High Score.

Chemical analysis

Chemical analyses were obtained by inductively coupled plasma atomic emission (ICP-AES) and mass spectrometry (ICP-MS). ICP-AES was used to determine Na, K, Ca, and Mg, Fe and Si concentrations and ICP-MS for Al. The method consists of weighing 0.1 g of overdried material into a container for digestion in an excess acid mixture consisting of 15 ml HF, 2 ml HCl,

2 ml HNO_3 and 2 ml H_2O . Loss on ignition was determined gravimetrically by heating powders up to 1000 °C for 1 h. The detection limit for main elements is 0.01 wt%.

Evaluation of plasticity

The evaluation of plasticity was performed by the Atterberg limits method (L.C.P.C, 1987) [8]: lower plastic limit (LPL); upper plastic limit (UPL) and plastic index (PI). The plasticity index (PI) was calculated basing on the arithmetic difference of the LPL and UPL of clays. The LPL and UPL tests were carried out with a Casagrande apparatus using the method described by Casagrande [9] and by Grim [10]. A simulation of the industrial processing was performed on a laboratory scale: dry grinding was carried out by jaw crushing, and hammers milling. These powders were wetted and mixed with an amount of water slightly above the plastic limit, in order to achieve the proper plasticity for the extrusion processes.

Dilatometry test

The firing characteristics of the raw clay were determined by heating the sample up to 1000 °C using an ADAMEL LHOMARGY, DM 15 dilatometer. The samples ($65 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$) were semi-dry pressed from the powders (fraction $< 100 \mu\text{m}$). The pressed samples was dried overnight at 40 °C then heated in horizontal-expansion dilatometer between 25 and 1000 °C at a heating rate of 10 k/min.

Length changes were recorded every minute during the heating stage. The accuracy of dilatometry instrument is $\pm 0.1 \times 10^{-6} \text{ }^\circ\text{C}$, for the expansion coefficient obtained over a 100 °C temperature interval.

Industrial processing

The obtained mixtures M1, M2 and M3 were humidified (6.5 wt% moisture content) and sieved to pass through 1 mm screen in order to obtain suitable powders for pressing. Samples with dimensions $100 \times 50 \times 5 \text{ mm}$ were uniaxially pressed at 25 MPa. The shaped samples were dried so the free water content was subsequently eliminated through heating at temperature of 110 °C for 24 h until a constant weight was achieved.

The pieces were finally heated to 850, 900, 950, 1000 and 1050 °C and kept at the maximum temperature for 1 hour within a firing cycle of total 4 hours which include cooling in electrical laboratory chamber kiln. The chosen temperatures are typical for temperatures of industrial faience ceramics.

Fired products were determined using firing shrinkage, water absorption, loss on ignition and the bending strength. The latter was carried out using a three point bending test using the French standard NF EN 100-82' [11]. The dimensions of the pressed

Table 1. Mineralogy of Triassic deposits' samples estimated by XRD analysis (wt %)

	Illite (%)	Kaolinite (%)	Quartz (%)	Dolomite (%)	Hématite (%)
M1	40	10	15	30	5
M2	31	8	51	10	-
M3	53	12	25	-	10

specimens were measured before and after firing in order to determine the firing shrinkage ($100(L_d - L_f)L_d^{-1}$, where L_d represented the length of the dried specimen and L_f the length of the fired specimen at various temperature). The water absorption values, determined according to the EN 99 [12] standard, were calculated from weight differences between the as-fired and water saturated samples (immersed in boiling water for 2 h).

Bending strength was calculated by: $\sigma_f = 3FL / 2bh^2$ in which F = breaking load (in kg), L = distance between supports, b = sample width and h = sample thickness (all in mm). Each value represents the

average of measurements made on ten individual specimens.

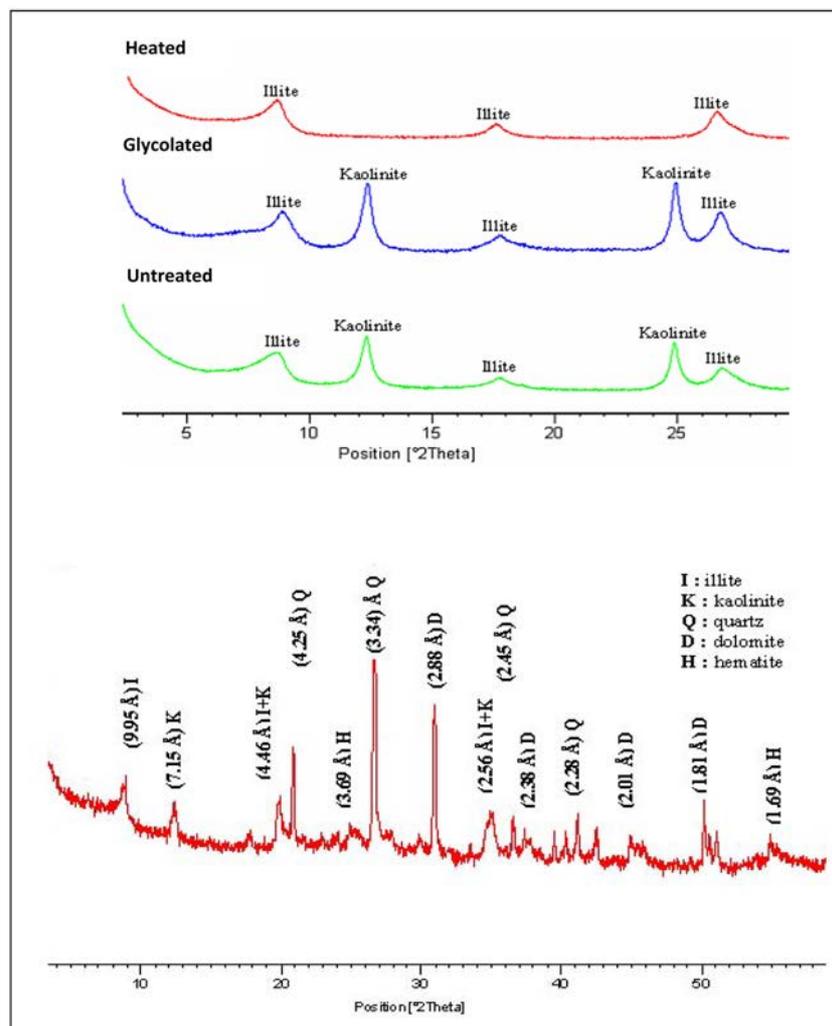
Results and discussion

The mineralogical composition of clay mixtures, summarized in Table 1, indicates that the mineral association is the same in all cases and corresponds to the mixture of kaolinite, illite, and quartz (Fig. 2, 3, 4). These different clay raw materials do not present great differences in mineralogical and geochemical compositions.

The mineralogical composition is dominated by illite and quartz with lesser amounts of kaolinite. The illite presents favourable properties for ceramic use. The three samples contain high quantity of potash, indicative of the amount of illite.

The content of quartz is tolerable since it can be easily digested by vitreous flow during firing.

The clays have a definite illitic character (31-53%), these materials can be defined from a mineralogical point of view as illitic clays with a high sand content.

**Fig. 2.** X-ray diffraction of raw mixture M1, its oriented clay fraction: untreated, glycolated and heated at 550 °C

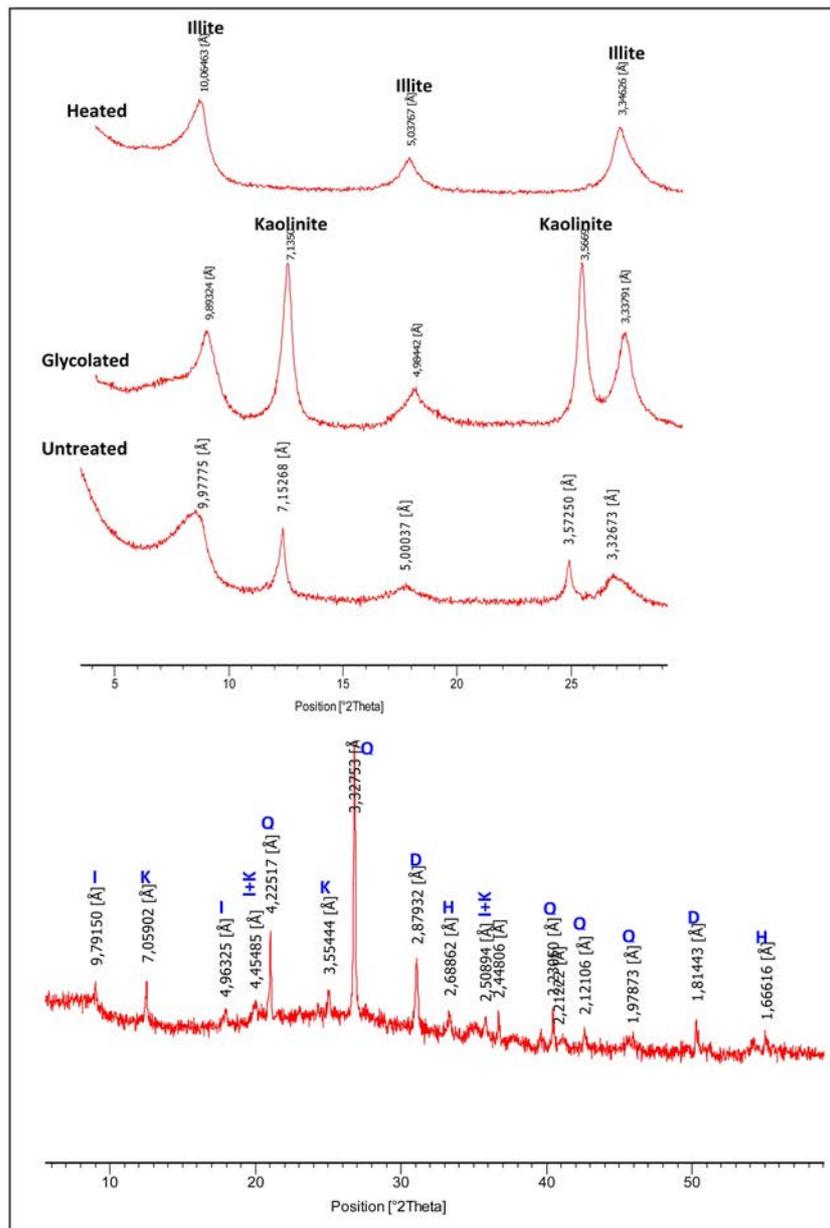


Fig. 3. X-ray diffraction of raw mixture M2, its oriented clay fraction: untreated, glycolated and heated at 550 °C

Table 2 show the chemical composition in terms of oxide contents and the loss on ignition for raw powder clay mixtures. These clays show the expected typical compositions, rich in silica and alumina; because of the presence of clay minerals and quartz, they have a decisive influence on the refractoriness and mechanical resistance of the final products. These oxides are accompanied by a significant amount of iron oxide, which is responsible for a dark color of the fired pieces [13]. Fe_2O_3 is not the only factor responsible for the coloring of ceramic products, other constituents such as CaO, MgO, Na_2O and TiO_2 can appreciably modify the color of the fired clay [14]. Moreover, the presence of large amounts of flux as well as Fe_2O_3 increases the chance to form a considerable amount of liquid phase at a relatively lower firing temperature.

Another important aspect with respect to the chemical composition of the clays is the high amount of K_2O that is considered the main flux agent of clay materials [3].

The high ignition loss (LOI) is attributable to the presence of substantial volatiles [15], comprising in clay minerals, of dolomite (carbonate), and organic matter.

The plasticity index and liquid limit (Table 3) of all the mixtures indicates that these clays belong to the filed illitic clay. A Casagrande diagram based on the above data (Fig. 5) demonstrates that all samples have satisfactory extrudability and a medium plasticity. On the other hand, the high content of quartz and the lack of clay minerals are the main factor for the low plasticity of mixture M2.

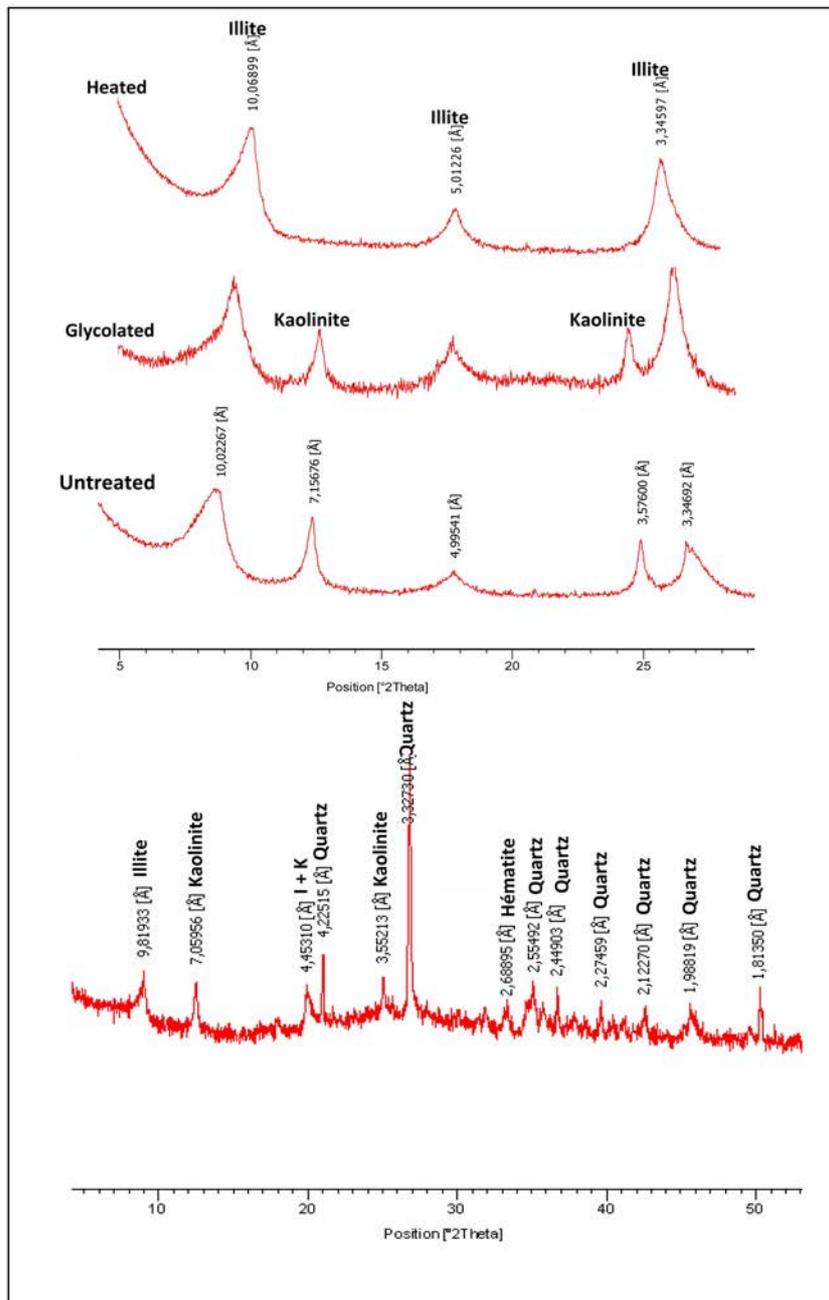


Fig. 4. X-ray diffraction of raw mixture M3, its oriented clay fraction: untreated, glycolated and heated at 550 °C

Table 2. Chemical compositions (wt %) of clay raw materials mixtures

Sam ple	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₄	P.F
M1	50,2	18,0	7,8	3	4,0	0,27	3,9	0,81	0,1	10,0
M2	59,3	12,7	6,4	3,3	3,2	0,09	2,6	1,24	0,22	10,1
M3	55,2	19,1	8,9	0,11	1,63	0,45	4,85	0,92	0,26	7,9

For practical purposes, the plasticity index must be above 10%, clays that present values of PI lower than 10% are not appropriate for building related ceramic production [16], due to the risk of problems during the

Table 3. Atterberg parameters of M1, M2 and M3

Clay	M1	M2	M3
Liquid limit	39	42	39
Plastic limit	29	28	26,5
Index of plasticity	10	14	12,5

extrusion process causing cracks in the green pieces.

The dimensional changes observed after firing of the studied clay mixtures (Fig. 6) show that all these clays display the polymorphic α - β transition of quartz at 573 °C.

A rapid expansion between 550 °C and 573 °C

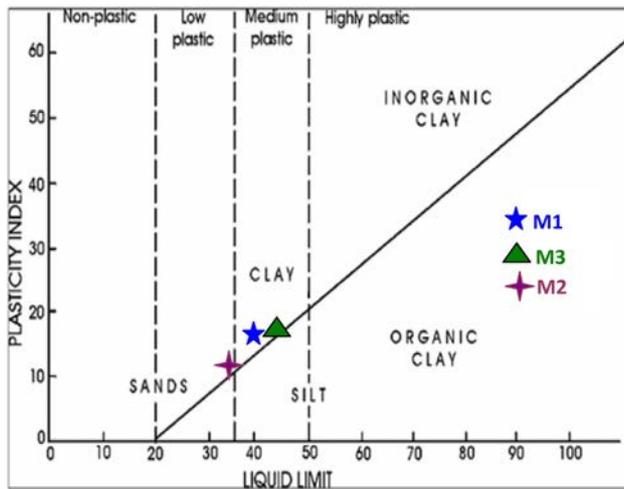


Fig. 5. Location of M1, M2 and M3 on the Casagrande chart.

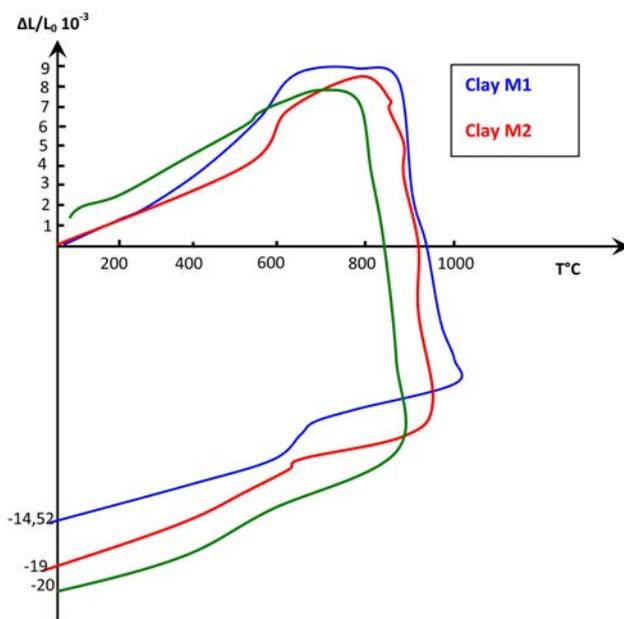


Fig. 6. Dilatometric curves of M1, M2 and M3.

corresponds to the dehydroxylation of the clays. This typical clay behaviour is characterised by an expansion at 600-900 °C, followed by a strong shrinkage due to the carbonate decomposition and loss of structural water.

The expansion values are 0.95% for M1, 0.90% for M2 and 0.74% for M3. The expansion is accompanied by a rapid shrinkage due to the vitrification. The presence of Fe₂O₃ and K₂O accelerates the vitrification [4].

Industrial tests

Three mixtures of clays were prepared from the Triassic clays M1, M₂ and M₃ had almost the same properties in drying shrinkage. In the drying step, it is adequate to obtain a value of drying shrinkage between 0 and 0.5% /l in order to avoid microcracks around sand grains.

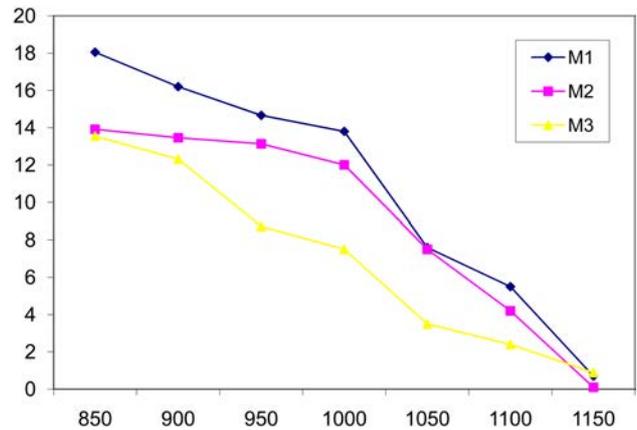


Fig. 7. Water absorption evolution of clay mixtures during firing tests.

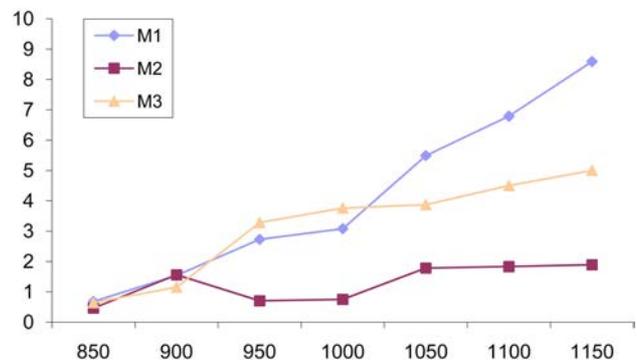


Fig. 8. Shrinkage of clay mixtures during firing tests.

The result concerning the test of water absorption as a function of temperature (Fig. 7). Comparing sintering temperatures of 850 °C with 950 °C, water absorption decreases from 13.54 wt% to 8.72 wt% in mixture M₃, in accordance with the refractory behaviour of clay. The water absorption is closely related to densification. Water absorption is the parameters which according to EN 100 [6] defines the class to which any faience ceramic product belongs. The bodies presented values indicating their conformity to normative class BIII.

The results of the physico-chemical properties indicate that the Triassic clays present only a moderate change in the fired properties from 850 to 1000 °C. However, above 1050 °C significant changes can be observed such as an increase in the linear shrinkage and flexural strength together with a decrease in the water absorption. This high temperature behaviour is associated with the sintering mechanism that promotes the densification of the samples, reducing the porosity. This behaviour can mainly be explained by the higher content of alkaline-earth elements (MgO and CaO), particularly the influence of MgO containing raw materials, such as dolomite, as sintering promoters on the vitrification. Increasing the temperature causes both an increase in the amount of liquid phase and a decrease in the liquid phase viscosity. Under the surface energy forces created by the fine pores

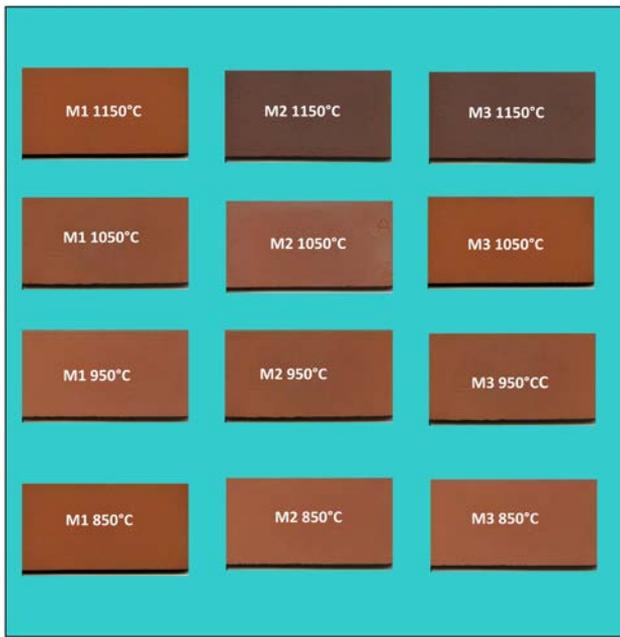


Fig. 9. Faiences Ceramic samples manufactured from clay mixtures.

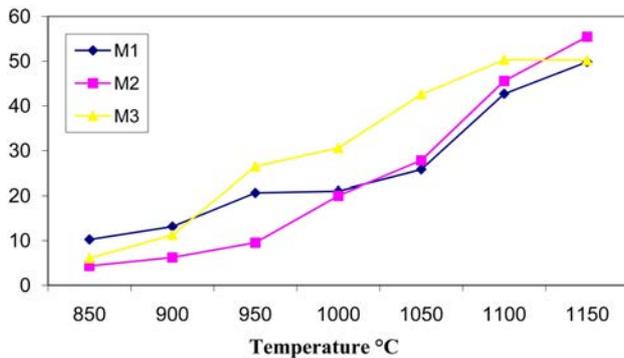


Fig. 10. Bending strength (N/mm²) determined on fired clay mixtures.

contained in the ceramic body, the liquid phase tends to approach the particles and therefore the open porosity decreases. Simultaneously, the closed porosity increases when the temperature is increased. The closed porosity is due to larger, isolated and spherical pores. Figure. 8 display an increasing of the firing shrinkage with increased firing temperatures, for all mixtures. Above 950 °C, M₃ shows a change associated with a more significant liquid phase formation. This phase penetrates the pores, closing them and isolating neighboring pores. This explains the intense decrease of the water absorption in this temperature range.

The firing temperature is an important factor enhancing the mechanical resistance and durability of end products in faience ceramic, as the material becomes denser. This is also an important engineering quality index for building materials. This effect is due to the progressive formation of calcium silicates and the melt phase filling porosity [17], in addition to the high fines content of the raw materials ensuring good

compaction during moulding. The color is red for all samples (Fig. 9), getting darker with increasing temperature due to the high concentration of iron oxides content [18]. In fact, mechanical bending resistance for M₃ increases from 6.06 after firing at 850 °C to 26.46 N/mm² when fired at 950 °C, with similar values for M₁. In contrast, no such difference is observed between for the M₂ mixture (Fig. 10).

The relatively high mechanical properties of glazed ceramic products are essentially due to their structure which is mainly composed of calcium silicates and aluminates as well as MgO in an amorphous state. The presence of a crystalline phase in the ceramic matrix provides the piece with a high fired mechanical strength.

Between 850 and 1000 °C, sintering process takes place, which consists in the aggregation compaction of particles. At 1000 °C, the higher porosity is connected with dense zones, resulting from carbonate decomposition with the evolution of CO₂.

Between 1050 and 1100 °C considerable decrease in the porosity occurs, coinciding with the beginning of vitrification. The densification behaviour of the Triassic red clay is influenced by the sources of flux materials such as K₂O, Na₂O and Fe₂O₃, which favour the formation of a vitreous phase [19].

At 1100 °C the porosity starts to reduce, when a liquid phase is present. At 1150 °C, the bodies showed advanced sintering, in this state, the open porosity has been reduced and spherical isolated pores can be observed, which could explain the great advance in mechanical properties with a decrease in the pore fraction [20, 21].

Conclusions

The results obtained for the materials studied indicate that from the point of view of their firing characteristics and chemical composition, they are suitable for the manufacturing of red ceramics faience. The results from the chemical analysis of the raw mineral powders show that the major oxides are Al₂O₃ and SiO₂, since they have a decisive influence on the refractoriness and strength of the final product. The large amount of quartz directly influences the quantity of the amorphous phase after firing [21].

During sintering, several phase transformations occur in the minerals present in the clay powder. This behaviour suggests that a sintering process occurred, leading to an improvement of the ceramic properties.

The medium plasticity of these clays resulted in a lesser amount of water being required for the extrusion process; the reduction in the drying linear shrinkage brings several advantages these are: a faster drying process, a decrease in energy consumption, and a smaller risk of developing cracks and dimensional effects.

The relationship between the mineralogy of the raw materials and phase changes taking place during their sintering under different conditions has been examined. Between 900 and 1000 °C a sintering process takes place, which consists in the aggregate compaction of particles. This process is not complete, so the ceramic pieces are still quite porous. At 1000 °C destruction of illites and their recrystallisation occurs between 1050 and 1100 °C a considerable decrease in the porosity occurs, coinciding with the beginning of vitrification. At 1150 °C the porosity decreases significantly. The reduction of porosity is linked to an increase in the bending strength of the clay matrix at the same time as the thermal expansion of the ceramic pieces increases.

It is expected that the present investigation will help to improve knowledge on the main clays as well as to contribute to a correct exploitation of the deposits and to facilitate an optimization of red faience ceramic fabrication.

References

1. F. Jamoussi. Ph.D. Thesis, The University of Tunis El Manar, 2002.
2. Baccour, H., Medhioub, M., Jamoussi, F., Mhiri, T., Daoud, A., 2008. Mineralogical evaluation and industrial applications of the Triassic clay deposits, Southern Tunisia. *Mater. Charact.* 59, 1613-1622.
3. Baccour, H., Medhioub, M., Jamoussi, F., Mhiri, T., 2009. Influence of firing temperature on the ceramic properties of Triassic clays from Tunisia. *J. Materials Processing Technology* 209 (6), 2812-2817.
4. Sousa S, Holanda J, Development of red wall tiles by the dry process using Brazilian raw materials. *Ceram inter* 2005; 31: 215-222.
5. D.M Moore, R.C. Reynolds in *X-ray Diffraction and the Identification and Analysis of Clay Minerals* (1989).
6. Thorez, Carreaux et dalles céramiques, Détermination de la résistance à la flexion p. 7 (1982).
7. Holtzapffel, Carreaux et dalles céramiques, Détermination de l'absorption d'eau p. 6 (1982).
8. P. Fisher in "Some comments on the color of fired clays". *Ziegel industrie International.* 37 (1984) 475-483.
9. R. Kreimeyer in "Some notes on the firing color of clay bricks". *Appli Clay Sci.* 2, (1987) 175-183.
10. A.H. Rankin, M.F. Miller and J.S. Carter. *Mineral Magazine.* 51 (1987) 517-525.
11. S. Sousa, J. Holanda. *Ceram inter.* 31 (2005) 215-222.
12. S. Monteiro, C. Vieira. *Appli Clay Sci.* 27 (2004) 229- 234.
13. C.M.F. Vieira, R. Sa'nchez, S.N. Monteiro. *Const and Build Mater.* 22 (2008) 781-787.
14. J. Parras, C. Sanchez-Jimenez, M. Rodas, and F.G. Luque. *App Clay Sci.* 11 (1996) 25-41.
15. H.M. Hassan Darweesh. *Cera Internation.* 27 (2001) 45-50.
16. H. Hassan, Darweesh. *Ceram inter* 27 (2001) 45-50.
17. K. Swapan, D. Kausik, S. Nar. *Appli Clay Sci.* 29 (2005) 137-143.
18. Hajjaji M., Kacim S., Boulmane M. *Appli Clay Sci.* 21(2002) 203-212.
19. K. Traoré., T.S Kabré., P. Blanchart. *Ceram Interna.* 29 (2003) 377-383.
20. Traoré K., Kabré T.S., P. Blanchart. *Appli Clay Sci.* 17(2000) 279-292.
21. E. Kamseu, C. Leonelli, D.N.Boccaccini, P. Veronesi, P. Miselli, G. Pellacani, U. Chinje *Ceram Inter.* 33 (2007) 851-857.