

Densification Behaviour of a Red Firing Tunisian Triassic Clay

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Abstract: Investigations were undertaken to assess the thermal modification in clay products from Triassic sedimentary deposits. This study deals with the mineralogical, physico-chemical, thermal analysis and faience making attributes of representative Triassic clay in the south-Eastern Tunisia. The data collected from these techniques show that illite and kaolinite are the major clay phases. The accessory minerals detected in powdered rock are; quartz, dolomite and hematite. The faience samples were dried pressed and sintered at temperatures ranging from 850 to 1150°C. The densification was measured by three parameters: firing shrinkage, water absorption, and resistance to the inflection. The development of resistance to the inflection and reduction in water absorption on samples products from this Triassic clay material was noticed at elevated temperatures due to enhanced vitrification. Large amount of iron oxides shows rapid vitrification and fusion during firing. Higher proportions of finer particles in the raw material also favour vitrification due to the good compaction of samples during moulding, this is has a positive influence on resistance of fired samples. Given the mineralogy and physicochemical characteristics of this clay could be used for the manufacture of faience ceramic.

Keywords: Tunisian, clay, ceramic, firing

INTRODUCTION

Clays are used as raw materials in many industrial fields (ceramics, paper, paint, petroleum industry, catalysis...) [1-2]. Their applications are tightly dependent upon their structure, composition, and physical attributes [3]. The knowledge of these characteristics can help for a best exploitation and eventually may open-up new areas of application. Clays are widely used in the manufacture of many traditional ceramics. Each ceramic product requires clays having particular and appropriate characteristics, they must not contain a swelling phase, their loss of weight and shrinkage, after drying firing, have to be low [4]. Clay bodies undergo several changes during drying and firing stages as a result of physical, chemical and mineralogical modifications. Kaolinite-illite is the most widely used clay mixture in the ceramic industry. Illite is one of the main clay phases used for the preparation of mixtures for traditional ceramics. The knowledge of the mineralogical phase composition of the raw materials used for the preparation of ceramic mixtures is of principal importance for understanding of the technological properties of ceramic products and optimizing of firing cycles in production. Potential source of clay materials for ceramic industry was discovered in Southeast Tunisia; there are extensive Triassic sedimentary clay deposits. In this presented study, a detail characterization of these clays is reported including their possible application in faience ceramics

production. The Tunisian production of ceramic faience has presented a rapid growth since 2000; in addition, the Tunisian production can grow still more due the high internal demand and opportunities for growth of the exportations. Although there is a great commercial interest in ceramic faience, very little research has been conducted in Tunisia in developing of ceramic faience. Within this context, the present paper discusses, in detail, the processing of faience ceramic using Triassic raw materials from Southeast Tunisia.

MATERIALS AND METHODS

Sample preparation: This study deals with the chemico-mineralogical characterisation and technological properties of both red clays raw materials (TRH₁ and TRH₂) collected from Triassic deposits in southern Tunisia (mountain Kirchaw). In order to assure representative sampling, not less than 50 Kg were collected from these deposits. After extraction, the clay was initially dried at 110°C, and then manually and gently crushed in order to reproduce particles without damaging the crystal lattices. The fraction < 2 µm was analysed on glass slides, according to Moore and Reynolds 1989 [5]. The fraction < 2 µm was obtained by centrifuging and then fraction collected by stake's setting. For clay mineralogical analysis, samples

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of these were dried at room temperature, other were glycolated for one hour solvated for detecting expandable minerals, and other 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].

Mineralogical analysis by XRD: 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 Cu-ka₁ radiation. Diffraction patterns between 3° and 60° (2θ) at a step size of 0.017°. Quantification of different phases was carried out by the logician X'-pert High Score.

Chemical analysis by ICP-MS: Chemical analyses were obtained by inductively coupled plasma atomic emission (ICP-AES) after LiBO₂ fusion 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. solutions were acidified by nitric acid to avoid precipitations of aluminium or iron hydroxides.

Plasticity: The evaluation of plasticity was performed by 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 based 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], Grim^[10], Minapuye^[11] and also described by Ekosse^[12].

Thermal analysis: The firing characteristics of the raw clay were determined by heating the sample up to 900°C using an ADAMEL LHOMARGY, DM 15 dilatometer. The sample (65 mm × 5 mm × 5 mm) was semi-dry pressed from the powder (fraction < 100 μm). The pressed sample was dried overnight at 40°C then heated in horizontal tubular furnace at heating rate of 10°C/min. The results of linear changes ($\frac{\Delta l}{l}$ %) were plotted as function of heating temperature.

Industrial processing: Mixture TRH with each of the raw clays (TRH₁ and TRH₂) was prepared and dried at 110°C for 24 hours, ground to fine powder. The obtained mixture was humidified (6.5 wt % moisture content) and sieved to pass through 1mm screen in

order to obtain suitable powders for pressing. The fine powder was humidified, homogenized and pressed in green ceramic faïences. 100×50×5 mm specimens were made. These specimens were initially with 6.5% moisture. The free water content was subsequently eliminated through heating at temperature of 110°C until constant weight was achieved. The pieces were finally heated to 850, 900, 950, 1000, 1050, 1100 and 1150°C and kept at the maximum temperature for 1 hour with thermal cycle of about 4 hours. The temperatures were arbitrarily chosen but correspond to temperatures used during the firing of industrial ceramic faïence. Unfired samples were characterised by the measurement of drying shrinkage and the mechanical resistance in flexion, on the fired products were determined: firing shrinkage, water absorption, weight loss in ignition and the mechanical resistance in flexion, carried out using a three-point bending test by respecting the French standard NF EN 100^[13]. The dimensions of the pressed specimens were measured before and after firing in order to determine the firing shrinkage: $100 \frac{(L_d - L_f)}{L_d} \%$ where L_d the length of the dried specimen and L_f the length of the fired specimen at different temperature. The water absorption values determined according to the EN 99^[14] standard, were calculated from weight differences between the as-fired and water saturated samples (immersed in boiling water for 2h).

RESULTS AND DISCUSSION

In order to assess their potentiality in the ceramic faïence industry, samples clay TRH₁ and clay TRH₂ were analysed from a chemical, mineralogical and technological view point.

Table. 1 shows the chemical composition in terms of oxide contents as well as the loss on ignition and the ions sulphates (SO₄) for both raw and purified mineral powders clays.

These two clays show the expected typical composition, 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 product. Those oxides are accompanied by a significant amount of iron oxide, which is responsible for a dark colouring of the fired pieces.

High percentage of FeO₃ may be attributed mainly to the presence of hematite, which was detected by XRD. Fe₂O₃ is not the only factor responsible for the coloring of ceramic wares, other constituents such as CaO, MgO, MnO and TiO₂ can appreciably modify the color of the fired clay. Moreover, the presence of large

Table 1: Chemical composition (W %) for studied clays

Clay	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₄	LOI
TRH ₁	52.3	20.5	7.8	0.06	1.55	1.5	4.3	0.81	0.1	9.7
TRH ₁ (<2μm)	74.8	23.3	9.7	0.06	1.8	0.55	5.0	0.82	0.07	10.2
TRH ₂	55.2	19.1	8.9	0.11	1.63	0.45	4.85	0.92	0.26	7.9
TRH ₂ (<2μm)	44.2	21.1	13.5	0.15	1.97	0.04	5.4	1	0.03	11.1

Table 2: Mineralogical composition of both TRH₁ and TRH₂ clays

Clay	Total rock mineralogy			Clay mineralogy	
	Phyllosilicates (%)	The non-clay minerals		Kaolinite (%)	Illite (%)
		Quartz (%)	Hematite (%)		
Clay TRH ₁	60	30	10	15	85
Clay TRH ₂	65	25	10	20	80

amounts of fluxes as well as Fe₂O₃ respectively increases to chance to form a considerable amount of liquid phase at a relatively lower temperature. The amount of alkaline oxides (K₂O and Na₂O) is high; the large amount of K₂O content in clay samples reflects the abundance of illite (Fig. 1 and Fig. 2) The high loss on ignition is associated with the presence of clay minerals, hydroxides, organic matter and volatile components.

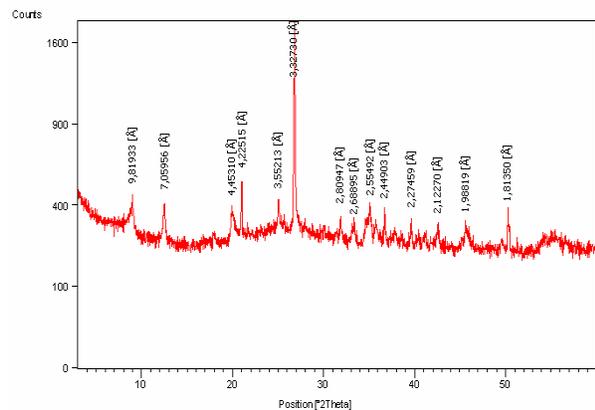


Fig. 1: X-ray diffraction pattern of the clay powder TRH₂

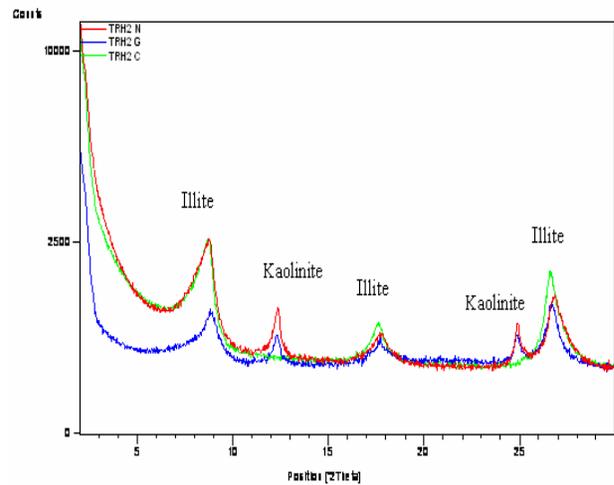


Fig. 2: X-ray diffraction pattern of the clay fraction TRH₂

Fig. 2 shows the X-ray patterns of the oriented clay TRH₂; it shows reflections at 7.07 and 3.57 which disappear after heating at 550°C. These reflections confirm the presence of the kaolinite phase. The peaks at 9.99 Å 5.00 Å and 3.33 Å are detected in the sample fraction; they are due to the presence of illite.

The studied samples show some interesting features for application in the ceramic sector if well treated especially considering the high iron oxide content. However, due to the generally high quartz contents they may possess a refractory behaviour. These clays have chemical and mineralogical compositions that indicate their usefulness for ceramic and faience production. The suitability of the clay material for ceramic faience products was assessed by determining the Atterberg limits.

The plasticity index PI was calculated based on the arithmetic difference of the LPL and UPL. Table 3 depicts the results of the plasticity tests, given by the Atterberg limits. One may observe that both clays present similar values of plasticity, which would be considered relatively medium according to the literature ($7\% < PI < 15\%$). It can be observed the values of the LPL at about 39 %, which are in agreement with the range defined in the literature (30-60%) to compositions used for ceramic production. Both clays also show high values for the lower plastic limit (LPL). This parameter has an important technological application, since it indicates the minimum percentage of moisture necessary to reach a plastic condition. With a high LPL there will be more difficulty in drying the samples.

The dimensional change observed after firing of the studied TRH mixture clay (Fig .3) can be described as follows: A slight expansion followed by shrinks between room temperature and 120 °C can be attributed to the less of the adsorbed water. A rapid expansion between 550 °C and 573 °C can correspond to several phenomena: dehydroxylation of the clay. The studied clay shows the allotropic transformation of quartz α to quartz β . A slight shrinkage starting at 800 °C is attributed to the formation of a vitreous phase. However a rapid shrinkage noticed above 870 °C can correspond to the vitrification of clay and as the resulting CaO reacts with the other oxides present, to form the new crystalline phases, this is most probable related to the formation of anorthite. TRH mixture clay raw materials containing low CaO do not show any expansion.

The results obtained from dilatometry curve show that between 870 and 960°C, the fusible phase appears mainly. The mean interval of temperature (90°C) gives the opportunity to the grains to react correctly between them and give materials that will resist to the deformation at high temperature, encouraging asset for the ceramic production. The presence of elevated content of Fe_2O_3 and K_2O alkali oxide in the clay raw materials may contribute to rapid vitrification. The

curve of dilatometry shows that Triassic mixture clays TRH will be charged until a temperature of 960°C.

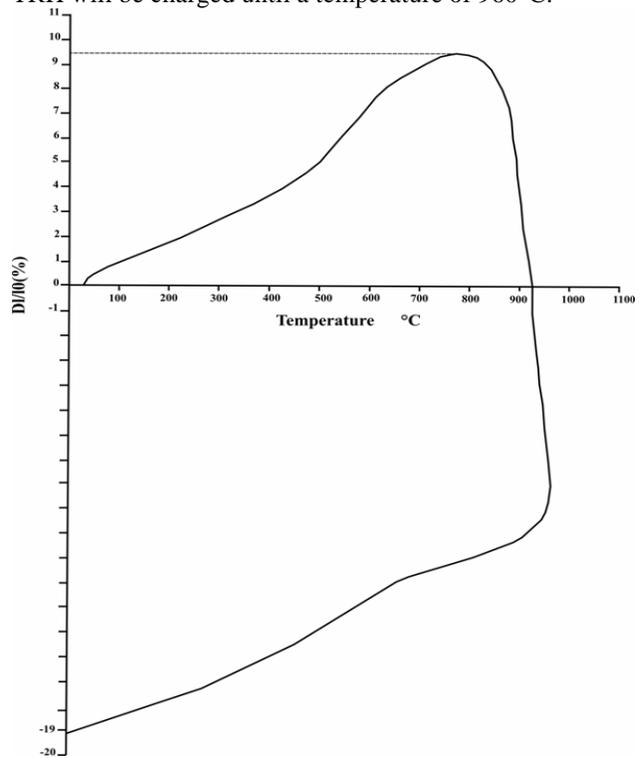


Fig. 3: Dilatometric curves of mixture TRH

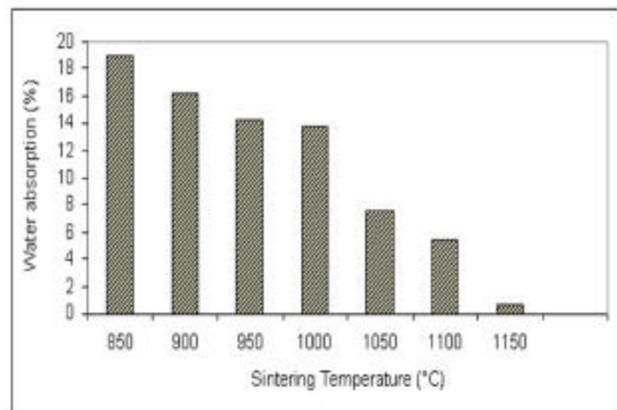


Fig.4: Water Absorption as function of sintering temperature

In the drying step, it is adequate to obtain a value of drying shrinkage between 0 and 0.5 % in order to avoid crack and fissures. The samples showed a slight expansion occurs after drying (0.3%). The slight expansion seems to be basically connected with their composition which rich in quartz (25%). The resistance to the inflection for dry samples equal 0.60 N/mm^2 , as

matter of fact, the poor mechanical resistance to the inflection and medium plastic of the Triassic clay are due to their abundance of silica minerals^[15].

Table 3: Plasticity parameters given by Atterberg indices (in wt. %)

Atterberg Clays	
indices:	
Clay TRH ₁	Clay TRH ₂
39	37
29	25
10	12

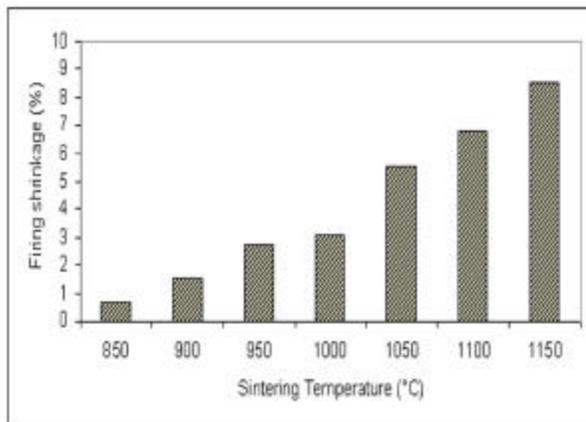


Fig. 5: Firing shrinkage as function of sintering temperature

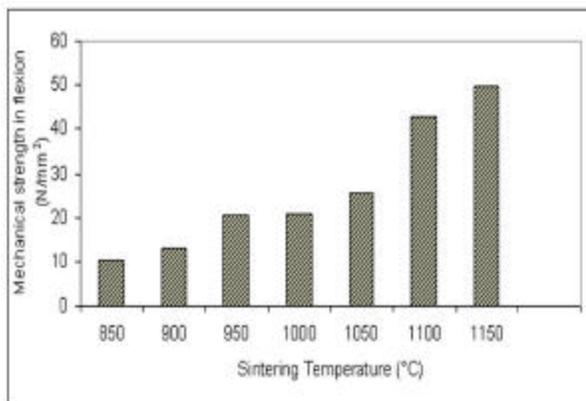


Fig. 6: Resistance in flexion as function of sintering temperature

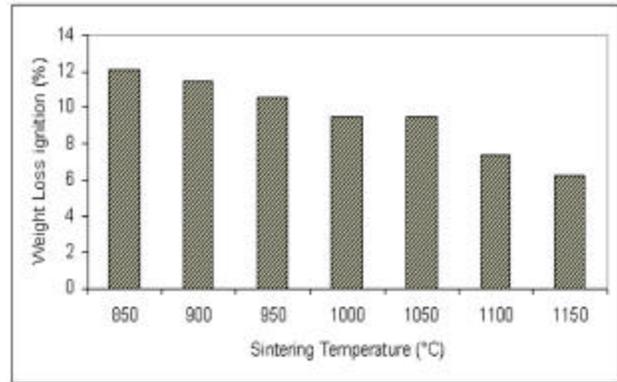


Fig. 7: Weight loss on ignition as function of sintering temperature

Water absorption is the parameter which according to EN 100^[13] definite the class to which any ceramic faience products belongs. The bodies presented values indicating their conformity to normative class BIII. The results concerning the test of water absorption in samples as a function of the sintering temperature shows that for sintering temperature of 1100 to 1150°C the water absorption is nearly zero (0.7%). It is well known that the water absorption is closely related to densification, and the amount of quartz influences the quantity of amorphous phase after sintering. However, the higher degree of sintering (water absorption lower) can be attributed to large amount of quartz in studied clay raw materials and impurity content. Above 1050°C the values of Water absorption decrease, that is associated with a more significant liquid phase formation. This phase penetrates the pores, closing them and isolating neighbouring pores. The liquid surface tension and capillarity help to bring pores close together and reduce porosity; this explains the intense decrease of the water absorption in this temperature range.

It can be seen that the ceramic bodies present a decrease in water absorption and an increase in firing shrinkage with increasing firing temperature (Fig. 5). This is a consequence of vitrification, which occurs during the sintering process helping to reduce porosity. Vitrification is a phenomenon associated with formation of liquid phase. By the action of capillarity and surface tension this particles undergo a rearrangement that promotes densification and contraction of the internal structure.

The mechanical resistance to the inflexion increases with vitrification up to high level of resistance, then the material becomes breakable. At higher temperatures when vitrification is completed, the pores join together to form large pores causing the macroscopic deformation on the ceramic materials by

bloating^[16]. The relatively high mechanical properties of ceramic faience products are essentially due to their structure which mainly composed of calcium silicates and aluminates as well as MgO in amorphous or crystalline state. This behaviour is due to the progressive formation of calcium silicates^[17] and also the higher fines of raw materials which gives the good compaction of samples during moulding, this has a positive influence on the mechanical resistance of fired samples. The effect of the temperature was to increase the resistance by means of densification. A colour is red for all samples, getting darker for increasing temperature due to the high concentration of iron oxides content^[18]. Above 950°C, the firing shrinkage ranges from 3.08 to 8.59 % (Fig. 6); in this temperature illite decomposition. The densification behaviour of the red clay is influenced by the sources of flux materials such as K₂O, Na₂O and Fe₂O₃, which favour the formation of vitreous phase.

The weight loss on ignition which occurs after sintering is related to the development of the porosity and the densification, and has an effect on the resistance to the inflection of the thermally treated samples, it is assumed that as the temperature was increased, the carbonate in clay become deformed into CO₂ (Fig. 7).

At 850°C, kaolinite is transformed into metakaolinite by the removal of the hydroxyl groups of the silicate lattice above 450°C. Between 850°C and 950°C, the CaCO₃ decomposes to CaO accompanied by the evolution of CO₂ outside the structure of fired bodies. The CaO reacts with the amorphous phase (metakaolinite) at increasing temperature, thus, the formation of crystalline phases as anorthite occurs to a great extent at the expense of the metakaolinite. According to the literature the structural iron favours the structural transformations of metakaolinite to gehlenite and then to anorthite. Initially the gehlenite non stable intermediate phase is formed from metakaolinite and calcium oxide. Later anorthite is formed from gehlenite, which is combined with silica and alumina rich phases due to the metakaolinite structure break and the residual fine quartz.

CONCLUSIONS

Representative Triassic raw material was characterised by chemical, thermal and XRD analysis. It appears that the clay used was illitic and kaolinitic type containing substantial amount of quartz in it. The results from the chemical analysis of the raw mineral powders show that the most important are Al₂O₃ and SiO₂, since they have a decisive influence on the

refractoriness and strength of the final product. For the chemical compositions the sum of Fe₂O₃ and TiO₂ is 8.72 %, many studies have described the influence of these mineralisers in enhancing the process of sintering of ceramic matrix and formation of mullite, Fe³⁺ and Ti⁴⁺ play important role by their substituting Al³⁺ or by their incorporation into the interstices of the matrix. This behaviour suggests that a sintering process occurred, leading to the improvement of the ceramic properties. The relationship between water absorption, shrinkage and resistance to the 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. We can affirm that gain in resistance and reduction in water absorption of fired samples largely depend on the mineralogical and mechanical make up of clay materials used in their production, besides temperature of firing. Representative Triassic mixture TRH clay sample, rich in minerals: oxides of iron, alkali and alkaline earths on exposure to elevated temperatures, generally show rapid vitrification and fusion during firing.

Higher proportions of finer particles in the raw material also favour vitrification due to the good compaction of samples during moulding, this has a positive influence on resistance of fired samples.

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

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