I O U R N A L O F

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Composition and ceramic properties of triassic clays from tunisia

M. Medhioub^a, H. Baccour^{b,*}, F. Jamoussi^c and T. Mhiri^b

^aLaboratoire Géoressources, Faculté des Sciences de Sfax 3018, Sfax-Tunisie. ^bLaboratoire de l'Etat Solide, Faculté des Sciences de Sfax 3018, Sfax-Tunisie. ^cLaboratoire Géoressources. CERTE, Bp.273, Soliman, 8020 Tunisie.

Investigations were undertaken to assess the thermal modification in clay products from the Triassic deposit (Southeast Tunisia), in order to use them in ceramic products. That is why the study had recourse to several quantitative and qualitative techniques of analysis; chemical analysis, a mineralogical study, thermal analyses and analyses of geotechnical traits. The geotechnical characterization was carried out on a representative mixture of Triassic clay. The samples were dry pressed on clay bodies and sintered at temperatures ranging from 850 to 1150 °C. XRD and SEM were used to identify the phases present and the densification level. The relationship between water absorption, shrinkage and resistance to inflection as a function of the firing temperature was examined in order to enhance the quality of the final products and to optimize the production process. The results revealed that sintering is governed by different mechanisms according to the temperature. The neomineralization processes were investigated principally by X-ray diffraction. At the end of this study one can affirm that these clays have qualities necessary for the manufacture of traditional ceramic products.

Key words: Tunisian clay, ceramic, thermal analysis, firing.

Introduction

Worldwide clays are the main raw materials exploited in the fabrication of diversified ceramic products for building construction [1], and have been extensively studied [2]. For this reason, particular attention should be given to the exploitation of raw materials in Tunisia for ceramic applications. The present paper aims at investigating a particular application of local clays collected from the Triassic deposit (Southeast Tunisia), to evaluate their potential for the manufacture of glazed ceramic production. Technological properties of a ceramic product are not only related to its mineralogical composition of the raw materials but also to the different variables in the production operations (drying, shaping, firing and thermal gradient) [3, 4].

Upon firing, minerals in clay bodies undergo chemical and structural modifications: dehydration, dehydroxylation, decomposition and the formation of new phases and vitrification. These processes are mainly influenced by the chemical and mineralogical composition of the original clay. Each raw material has a complex mineralogical composition. This makes the study of its thermal transformations rather difficult. In structural clay products, these changes are essentially brought in to enhance mechanical strength and durability properties. The knowledge about these transformations makes easier the control of the properties of the material [5]. Microstructural analysis of sintered samples, which is fundamental to interpret the corresponding mechanical properties, was conducted by SEM.

The Tunisian production of ceramic glazed ware has presented a rapid growth, but very little researches has been conducted in Tunisia in developing glazed ceramics. Within this context, the present paper discuses, in detail, the processing of glazed ceramics using raw materials from south eastern Tunisia. The local industries have empirically exploited these clay materials deposits. Nevertheless, there is little information on the characteristics and properties of these materials. As a consequence, the final products generally present negligible quality. However, it is a known fact that in industrial countries, a thorough physical-chemicalmechanical understanding of clay materials is considered the most essential stage before processing them into any ceramic product. Thus, it is very important to carry out an extensive characterization of these materials in order to gain more knowledge, which can contribute to obtaining of improved properties.

Materials and Methods

This paper reports the results of a study dealing with the chemical and mineralogical characterization and the firing behaviour of clay collected from the Triassic sedimentary deposit (Southeast Tunisia) (Fig. 1). In order to ensure a representative sample, no less than 50 kg of clay was collected from this deposit.

The mineralogy of the raw material, as well as its corresponding $< 2 \mu m$ fraction was determined by X-ray diffraction. The XRD patterns were obtained with an X'Pert

^{*}Corresponding author:

Tel : +21620264354

Fax: +21674274437

E-mail: hajerbaccour@yahoo.fr



Fig. 1. Location of the Triassic clay deposit studied.

Pro PANalytical diffractometer operating at 45 kV and 40 mA using Cu-k α_1 radiation. Diffraction patterns were between 3° and 60° (2 θ) at a step size of 0.017°.

The fraction $<2 \mu m$ was analysed on glass slides, according to Moore and Reynolds 1989 [6]: The fraction $<2 \mu m$ was obtained by centrifuging for 10 minutes; in addition, each sample was dispersed in distilled water, ultrasonicated to enhance dispersion, and the $<2 \mu m$ fraction collected by setting; a small amount of the claywater suspension was placed by pipette onto a slightly ground glass slide and left to dry in order to prepare oriented specimens. Crystalline phases were identified and evaluated by XRD and SEM.

Chemical analyses were obtained by inductively coupled plasma atomic emission (ICP-AES) and mass spectrometry (MS). The parameters of plasticity were determined in accordance with the French Standard NF P 94-051 [7]. Particle size distribution was determined by Laser particle analyser on the 0.1-100 μ m fractions.

A representative clay mixture was dried at 110 °C for 24 hours, ground to a fine powder, then was humidified and sieved to pass through a 1 mm screen in order to obtain suitable powders for pressing. To prepare fired samples, a homogeneous mixture of fine powder-water was pressed in green glazed ware. $100 \times 50 \times 5$ mm specimens were made. The free water content was subsequently eliminated through heating at a temperature of 110 °C until a constant weight was achieved. The pieces were finally heated at temperatures ranging from 850 to 1150 °C and kept at the maximum temperature for 1 hour with a thermal cycle

of about 4 hours.

Technological properties were evaluated for both, simply dried and fired specimens. 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 using the French standard NF EN 100 [8].

The dimensions of the pressed 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 the length of the dried specimen and L_f the length of the fired specimen at different temperatures. The water absorption values determined according to the EN 99 [9] standard, were calculated from weight differences between the as-fired and water saturated samples (immersed in boiling water for 2 h). The firing characteristics of the raw clay were determined by heating the sample up to 1000 °C using an ADAMEL LHOMARGY, DM 15 dilatometer.

Results and Discussion

In order to assess the potentiality of Triassic clay in the glazed ceramic industry, representative clay was analysed from a chemical, mineralogical and technological view point. Table. 1 shows the chemical composition in terms of oxide contents and the loss on ignition for raw powder clay. This clay shows the expected typical composition, rich in silica and alumina; because of the presence of Composition and ceramic properties of triassic clays from tunisia

Ignition Loss at 1000 °C.	
SiO ₂	50.20
Al_2O_3	18.80
Fe ₂ O ₃	7.80
CaO	3.2
MgO	3.9
Na ₂ O	0.30
K_2O	3.9
TiO_2	0.81
Ignition Loss	11

Table 1. Chemical composition (wt %) for the clay studied Ignition Loss at 1000 °C.

clay minerals and quartz, they have a decisive influence on the refractoriness and mechanical resistance of the final product. These oxides are accompanied by a significant amount of iron oxide, which is responsible for a dark colouring of the fired pieces [10].

A high percentage of FeO₃ may be attributed mainly to the presence of hematite, which was detected by XRD (Fig. 2). Fe₂O₃ is not the only factor responsible for the coloring of ceramic products, other constituents such as CaO, MgO, Na₂O and TiO₂ can appreciably modify the color of the fired clay [11]. Moreover, the presence of large amounts of fluxes as well as Fe₂O₃ increases the chance to form a considerable amount of liquid phase at a relatively lower firing temperature.

The value of the spell out is related to the dehydroxylation of the clay minerals, organic matter oxidation, and the decomposition of carbonates and hydroxides [12].

The large amount of K₂O content in clay samples reflects the abundance of illite [13] (Fig. 2). The following mineralogical phases were identified: illite as the principal mineral (characteristic peaks at 9.95 Å and 4.97 Å), with kaolinite (peaks at 7.2 Å and 3.58 Å) and quartz (peaks at 4.25 Å and 3.34 Å). Other secondary minerals phases found in this clay are hematite and dolomite. Rational mineralogical composition analysis showed that clay raw material contained: 61% phyllosilicates (kaolinite (35%); illite (65%)); quartz (25%); dolomite (10%) and hematite (4%).

Fig. 3 shows the X-ray patterns of the oriented clay; it shows reflections at 7.07 and 3.57 Å which disappear after heating at 550 °C. These reflections confirm the



Fig. 2. X-ray diffraction pattern of the clay raw material.



Fig. 3. X-ray diffractograms of the $< 2 \mu m$ fraction.



Fig. 4. Dilatometric curve of the Triassic clay.

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 dimensional change observed after firing of the clay studied (Fig. 4) is the slight expansion followed by shrinkage between room temperature and 120 °C, which can be attributed to the diminution of the adsorbed water. A rapid expansion between 550 °C and 573 °C corresponds to the dehydroxylation of the clay. The clay studied displays the polymorphic á-â transition of quartz at 573 °C.

A slight shrinkage starting at 750 °C is attributed to the formation of vitreous phases. After the decomposition of the carbonates, a rapid shrinkage was noticed above 860 °C which can be related to the vitrification of clay. The expansion value is 0.9% for this Triassic clay. The presence of Fe₂O₃ and K₂O accelerates the vitrification [14]. The final shrinkage is about 1.4%, the rate of shrinkage is relatively low because this sample consists mainly of illite and quartz.

Fig. 5 shows that the fraction below $< 2 \,\mu m$ is very high



Equivalent spherical diameter (µm)

Fig. 5. Granulometric analyses of Triassic clay.



Fig. 6. Position of the studied clay on the Holtz and Kovacs diagram.

for the Triassic clay powder. This particle size distribution is excellent for use in ceramics. Due to the size distribution the raw materials is classified as a silty clay and usable for ceramics products.

Fig. 6 shows that the crude a sample Triassic clay belongs to the filed of an illitic clay on the Holtz and Kovacs diagram [15]. The plasticity index was near 13% and the clay poor to moderate plastic properties [14]. On the other hand, the high content of quartz and clay minerals are the main factor for the low plasticity [3].

The results of the physico-chemical properties are presented in Table. 2. These results indicate that the Triassic clay presents only moderate changes 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.

Water absorption is the parameters which according to EN 100 [3] define the class to which any ceramic faience product belongs. The bodies presented values indicating their conformity to normative class BIII.

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 of crystalline state. The presence of a crystalline phase in the ceramic matrix provides the piece with a high fired mechanical strength.

At 700 °C CaCO₃ begins to decompose to CaO, this decomposition during firing is often accompanied by the evolution of CO_2 outside the structure of the fired samples witch tends to create a more porous structure [16]. The free CaO reacts with the amorphous phase derived from decomposition of illite, which diminishes at increasing firing temperatures [17]. The water absorption increases gradually due to the evolution of more CO_2 outside the structure.

Metakaolinite was formed from kaolinite by the removal of the hydroxyl groups of the silicate structure above 450 °C. Gehlenite is considered an intermediate compound [18], is crystallised from metakaolinite and calcium, which becomes unstable in the presence of SiO₂ and reacts to give anorthite CaAl₂Si₂O₈ according to the following reactions:

$$Al_2O_3$$
, $2SiO_2 + 2CaO \rightarrow Ca_2Al_2SiO_7$ (Gehlenite) (1)

$$Ca_2Al_2SiO_7 + 3SiO_2 + Al_2O_3 \rightarrow 2$$
 (Anorthite) (2)

The anorthite phase is tri-dimensionally dispersed in a silico-aluminate matrix, resulting in a significant increase of mechanical strength [19]. When the temperature is increased, the anorthite peak intensities begin to increase (Fig. 7) and the quartz peak intensities begin to decrease. X- ray patterns from this material sintered at 1100 °C indicate clearly the principal anorthite phase formation,

Table 2. Results of the physical parameters according to the sintering temperature of the Triassic clay

Temperature (°C)	Linear Firing shrinkage (LF) (%)	Water absorption (WA)(%)	Flexural strength (N/mm ²)	LOI (%)
850	0.54	17.05	10.55	13.08
900	1.44	15.20	14.20	12.05
950	2.66	13.22	19.55	10.02
1000	3.00	12.80	25.23	8.5
1050	5.06	6.60	30.44	7.43
1100	6.09	5.00	47.64	6.34
1150	7.59	0.50	50.20	6.02



Fig. 7. X-ray diffraction patterns for the mixed clay sintered at 1100°C.

from gehlenite is combined with aluminium and silicon from metakaolinite and the remaining fine quartz [20].

The sintering process in ceramics has been extensively studied and is to known to have a direct relationship with the microstructure. The correlation between microstructure and material performance was examined here.

Fig. 8 shows the microstructures of the ceramic bodies sintered at various temperatures. SEM micrographs, taken at increasing firing temperatures, show the progression of enhanced densification with increasing temperature. The scanning electron micrographs of the sample surfaces several the presences of microscopic pores and voids.

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 contained in the ceramic body, the liquid



Fig. 8. Microstructures of the ceramic bodies sintered at various temperatures.

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.

Between 850 and 1000 °C, a sintering process takes place, which consists in the aggregate compaction of particles. At 1000 °C, the higher porosity is connected with dense zones, resulting from carbonate decomposition with the evolution of CO_2 .

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 K_2O , Na_2O and Fe_2O_3 , which favour the formation of a vitreous phase [21].

At 1100 °C the porosity starts to reduce, when a liquid phase was present. At 1150 °C, the bodies presented 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 decrease in the pore fraction [13, 16].

Conclusions

The chemical and mineralogical composition of this red Triassic clay largely influences its technological properties, which determine its use in the ceramic industry and as building materials.

This study has shown that a higher temperature aids in increasing the consolidation and facilitates a homogeneous microstructure. The presence of a high content of Fe_2O_3 and K_2O in the samples fired at different temperatures accelerates the vitrification process, due to the fluxing effect of these oxides.

The amorphous silica liberated during the metakaolin decomposition or the impurities contained in the raw materials could also give rise to liquid phase formation. The optimal vitrification range is achieved when the open porosity reaches a minimum value, tending to be nearly zero and simultaneously linear shrinkage is a maximum. The large amount of K in the illitic clay mixture determines the formation of an alkaline melt which is an unfavourable chemical environement for cristobalite. As a consequence cristobalite has not been found in the fired products. The microstructure of sintered samples was imaged by a scanning electron microscope to determine the morphology and distribution of pores in the microstructure. The bodys shows a good sintering behaviour. The fired samples are homogenous and free of defects such as cracks. The homogenous distribution of the grains and pores is probably responsible for the particularly high strength.

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