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ECHNOLOGICAL VALORIZATION OF THE MIOCENE CLAY IN THE REGION OF FEZ (MOROCCO): CHARACTERISATION AND EXPLOITATION POSSIBILITIES

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Abstract. Given the increasing exploitation of clays in Morocco for the ceramic industry and other purposes, the present study aims to identify the characteristics of the Miocene clay in Fez area, based on the mineralogical, thermogravimetrical and technological analyzes.
The mineralogical analyzes show that the clay fraction is mainly composed of kaolinite and illite. Thermogravimetric analyzes and data collected from drift allow the apprehension of the evolution of the samples mass as a function of temperature and thus to establish an adequate idea on results of the firing program. Technological testing and other analytic data, allow the development of a basic abacus necessary for optimal use of clays in the brick making and in ceramic and / or pottery.

Introduction

The use of clay resources by human, mainly in the manufacture of building materials, dates from antiquity. The growing exploitation of clay-based materials in the ceramic industry results from the further knowledge of their physicochemical properties. Clay is a cheap and abundant material.

The Miocene clay substrates are abundant in the region of Fez, yet they remain insufficiently valued. However, considering the new demands of the society in terms of sustainable development and energy conservation, recovery of the clay and its use in building materials may be more environmentally sustained and become a scientific and industrial concern. It was investigated from different points

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of view (Fabri and Fiori, 1985; De Andres Gomes de Bared, 1990; Parras et al., 1996; Dondi et al., 1999; Gonzalez et al., 1999).)

The clays are widely used for diverse needs by the local population in Fez region. However, only few papers were published on these materials (Bouyahyaoui, 1996).

The present study apprehends the applied aspects of the clay use, mainly in the ceramic activities and pottery, on the basis of physico-chemical characteristics of clays and the results of technological testing.

The major problem encountered by users of these materials is the mastery of composition and sintering process of ceramic bodies, to improve the performance, efficiency and quality in manufacturing baked clay products. This work is undertaken to understand the influence of firing and temperature gradient on the mineralogical nature of clays; the results are analyzed in the light of quality norms imposed in clay materials for ceramics and related activities.

The use of clays in the industrial applications is dependent on the knowledge of their physicochemical properties and technology. For this purpose, several analytical techniques were used, especially X-ray diffraction analysis, thermal analysis, and geotechnical testing.

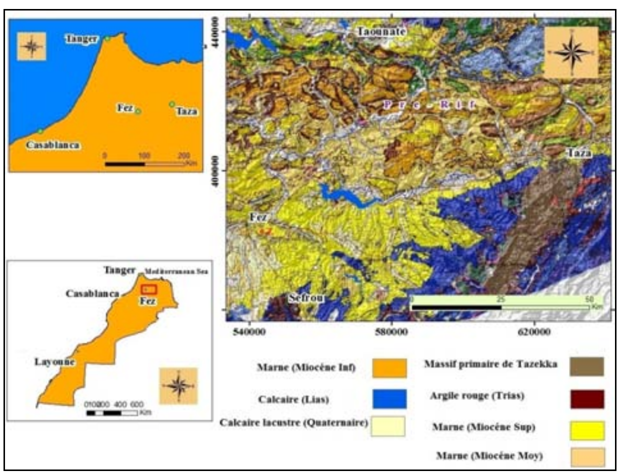

Fig. 1 -The location and geological map of Fez-Taza area (Morocco)

1. Materials and methods

1.1. Materials and substrates*:* This study is interested in the characteristics of three samples of Miocene clay (Fig. 2) which outcrop in the eastern area of Fez (Fig. 1) at the Ben Jallik quarry. These three samples Z1, Z2 and Z3 are located respectively in the lower, middle and upper stratigraphic series of Miocene clays (Fig.3). Their colors vary from gray-black for Z1, Z2 to yellow-beige for sample Z3. The extraction of clay in this quarry which is exploited for the bricks and the pottery activities is done in a traditional way.

The importance of clay-based materials in the ceramic industry is due to their plastic properties (Holtzapffel, 1985) allowing final ceramic products to retain their shapes after firing. The process is complex because usually the shaped product depends on the mineralogical composition of the raw material and the nature and quantity of impurities in clay. To explain these phenomena, several analytical techniques were used in the present study.

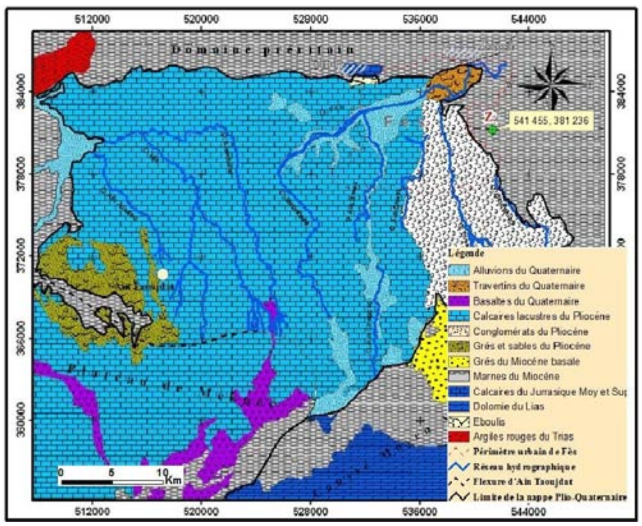

Fig. 2 - Geological Map of study area with samples location (ABHS)

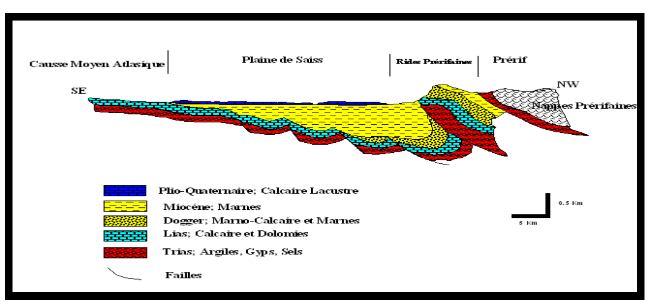

Fig. 3 - Geological cross section of South Rif (DRH et ONI, 1971-1977)

1.2. Methods: Mineralogical analysis was made by X-ray diffraction (XRD), using a device Philips XPERT-PRO "PW 3064, with radiation Kα1, 2 copper, performed on non-oriented powders, thermogravimetric analyzes and drift were made using a camera coupled DTA-TGA-type SETARAM with a heating rate of 10°C.min^{-1}.

The evaluation of plasticity was performed by the Casagrande method (Atterberg limits). These limits are conventional physical constants indicating the clay transition from plastic to liquid state (WL) and from the plastic to solid state (WP). The plasticity index, which represents the difference between the liquid limit and plastic limit, defines the extent of the plastic field of clay (in accordance with standard NF P 94-051).

Bricks' production is carried out using a metal mold, provided for the operation. It has a length of 50mm. Bricks are previously dried in the open air in accordance with standard NF XP P94-060-1, in accordance with standard NF P 94-051 - the stabilization of the withdrawal. They are secondly fired in an electric oven programmable to the temperatures of 900°C, 1000°C and 1100°C, with a bake cycle of 3 hours and a bearing of one hour and a half to the maximum firing temperature and a temperature rise rate of firing of 10°C/min.

The parameters resulting from the brick firing are observed such as the materials withdrawal along drying and firing, the ignition loss, the porosity and the mechanical resistance to compression.

2. Results and discussion

2.1. Mineralogical analysis*:* The phyllic part of these clays consists of kaolinite and illite as found in the light fraction of quartz and calcite.

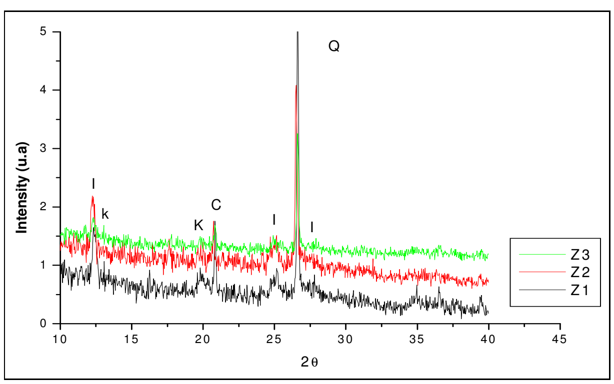

Fig. 4 - X.ray powder of natural clays marls. With K = kaolinite, Q = quartz; I = illite, C = calcite.

This is similar to natural mixtures encountered in traditional and modern ceramics where quartz is often added to clay minerals. In general, these minerals are important in the composition of marl clay for terracotta (bricks, tiles and pottery), because they promote the sintering in a low temperature (Khalfaoui, 2009). Quartz and calcite have an effect based in relation to other minerals. The kaolinite is particularly sought after, because of its refractory properties fairly well known. It has appreciable plasticity and low drying shrinkage. The absence of swelling interleaved in the clay and its ability to give slightly colored shards are appreciated. Kaolin clays are particularly suitable for the manufacture of quality ceramic product. The results show a predominance of illite and quartz that sustain the ceramic properties (El Yakoubi, 2006). The mineralogy of the three samples (Fig. 4) is similar and depends on a vertical homogeneity of the material. However, the proportions of mineralogical components vary, regarding on geotechnical testing.

2.2. Thermogravimetric analysis: The TGA thermogravimetric analysis spectra of samples (Fig. 5) show the following results:

-a first-grade between 50°C and 150°C corresponds to a weight loss of 2%. It is due to the evaporation of water absorbed and the zeolitic water (Trimdade, 2009),

-The second slope in the profile appears in the temperature range of 350°C and ends at 600°C. It shows significant thermal intensity and decomposition inducing active mass loss of 14% in the sample Z2 and 15% in Z1 and Z3. It reveals the first stage in the decomposition of organic matter at the temperature of 350°C, and the dehydroxylation of the OH groups of iron, silicate layers and carbonate at 300°C and 700°C (Jouenne, 1985).

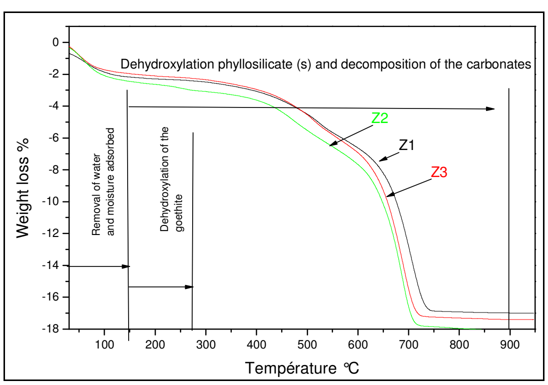

Fig. 5 -Thermogravimetric curve of samples

This behavior illustrates the presence of two types of clay sheets that differ in their mineralogical components. The total mass loss during the heating period, for a temperature not exceeding 800°C, is 16.59% for Z3, 17.30% for Z1 and 17.83% for Z2. Slight variations are observed beyond this temperature.

2.3. Technological testing. The marl samples tested are characterized by a dominant proportion of fine particle size. They show a percentage between 95 to 99% for elements less than 80 mμ in yellow clay marl (Z3) and in the grey clay marls (Z2 and Z1) respectively. Over 50% of these grains have a diameter smaller than 80 microns.

Tab. 1 – The results of plasticity analysis and water content in the samples

Sample	**Water content (w)**	**Liquid limit (Wl)**	**Plastic limit (Wp)**	**Plasticity index (Ip)**
Z1	20.1	43,2	19,40	23,8
Z3	21.2	60	27,16	32,84
Z2	20.6	46,6	23,02	23,58

Based on the results of Table 1, we note that the grey clays marls (Z1et Z2) show an intermediate plasticity. The yellow clay marl (Z3) have a high plasticity and is more suitable for the use in pottery.

Effect of firing

During the rise of the firing temperature (Table 2), physico-chemical transformations of the clay phase affect the material. Each mineral in the mixture behaves as if it were alone, however, its decomposition products, or new structural varieties, which arose under the influence of heat, react together to form new compounds.

A high shrinkage of 4.54 and 4.65% is observed at 900°C. It is related to an important development of the glass phase due to the importance of quartz (Baccour, 2011) and calcite in the material. This is consistent with the results of X-ray showing that the withdrawal reaches its maximum at 900°C and then tends to stabilize towards the higher temperatures of cooking (1000 and 1100°C). Therefore, the reduction in the material volume is usually due to the gradual disappearance of the porosity, as evidenced by low values of porosity at this temperature (900 °C) in connection with a high compressive strength.

Generally, the weight loss is attributed to dehydration, under the action of temperature on the mineral species. The quantification of the proportion of the weight loss of each mineral species is very difficult to assess in relation to the nature of the species, their proportions, their state of alteration, especially in a mixture of several mineralogical components. Samples lead after each firing at almost the same range of brick (Jouenne, 1984) beautiful red color appreciated in pottery and ceramic industry.

Tab. 2 - The firing impacts on the samples characteristics: porosity, loss on ignition and compression strength for the different processing temperatures

Sample	**T (C°)**	**Firing shrinkage (%)**	**Weight loss (%)**	**Porosity (%)**	**Compressive strength (bar)**	**Colors**
Z1	900	4.54	18,16	16.8	522.49	Beige
	1000	0.87	18,84	23	441.92	Red brick
	1100	1.31	18.00	19.71	434.72	Red brick
Z2	900	4.54	18,20	14.38	680.87	Beige
	1000	0.61	18,73	16.16	581.48	Red brick
	1100	0.65	19.58	13.71	520.14	Red brick
Z3	900	4.65	18,26	13.63	661.80	Red brick
	1000	0.77	18.56	17.43	351.82	Red brick
	1100	1.10	18.12	10.2	498.25	Red brick

Conclusion

Technological tests show that the Miocene marl clay from Fez area contains variable proportions of clay minerals with dominant kaolinite and illite. The non-clay minerals appear, such as quartz and calcite. These tests prove suitable industrial properties of these marls: an interval of sintering at 900°C using a baking temperature and low resistance to very high compression which is a very favorable factor in the use of this marl ceramic; the average loss on ignition and the firing shrinkage are acceptable (Ferrari, 2006). All samples show a significant plasticity, thereby promoting their possible use in pottery.

These interesting results confirm the possibility of using these clays marls in the ceramic industry. The local context favors the activity considering its important reserves of clays marls.

Acknowledgement

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