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Physicochemical and mineralogical characterizations of clays from Fez region (basin of Saiss, Morocco) in the perspective of industrial use

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Abstract

This study investigates on two gray clays used traditionally in the ceramic industry of Fès region and belonging to Saiss Basin (Morocco). They were sampled and characterized from their physical, chemical, mineralogical and ceramic stand points to evaluate their potential suitability as raw materials in various ceramic applications. Both clays, easily recognized by local experienced artisans, present different aspects although they were extracted from the same deposit and even from the same blocks: a smooth one with a dense aspect (FS1) and a grainy clay (FS2). Both clays showed similarities for thermal behavior, chemical composition and XRD diagrams. Both rocks are mainly composed by quartz, calcite, smectite, kaolinite and illite as dominant mineral phases while chlorite and some mixed layers were identified as minor phases.

Physical, mineralogical, chemical and thermal properties showed the complementarily of these clayey materials and justified the reasons for their using in the local traditional ceramic industry. Suitable formulations that depend on the type of the fabricated pottery (zellij, housewares or decoration articles) were discussed. According to their interesting properties, perspective of their use as membrane supports for filtration of wastewaters is pointed out.

Keywords: Moroccan clay, Plasticity, Ceramic technology, Saiss Basin.

1. Introduction

Clay industries are nowadays well developed. Clays have been widely used as the main raw materials in the fabrication of diversified ceramic products for construction materials such as bricks, fired clays, red stonewares, floor tiles, etc [1-6].Clays are also used as raw materials in many industrial areas such as paper, paint, petroleum industry, clarification of various effluents, catalysis, etc. Their applications are tightly dependent on their structure, composition, and physical properties. Knowledge of these properties is so important for understanding the technology of ceramic production. Furthermore, numerous traditional uses of clays find their justification thanks to their low cost.

The use of clays in pottery ceramics was the most widespread application of clays. In Morocco, clay is an abundant raw material with a variety of structures and compositions that correspond to many physical properties and consequently a very attractive use in many areas. Unfortunately, traditional methods of ceramic production are still not based on scientific knowledge. The clay mineralogy is one of the key factors determining the behavior of a ceramic body during production and processing, and the properties of the fired piece. The proportion, particle size and plasticity of the clay minerals will directly influence the characteristics of the ceramic body.

In lack of detailed studies of clays of this basin a research program dealing with the characteristics (mineralogy, chemical and physical properties) has been undertaken by our laboratory in order to enhance and extend their potential applications. In other areas of Morocco, also few is known about characterizations of clays for suitable applications [7-13].

The main objective of this paper is the study of the physical, mineralogical, thermal properties and secondly to check the applicability in the ceramic industry of the clays belonging to this region.

In the perspective of a sustainable development of the region, our laboratory, has an important experience in the valorization of local natural substances especially clays [14-17], perlite [18], pozzolan [19] and natural phosphate [20-22]. Recently, we started to evaluate Moroccan clays from the same Basin: Clay from Meknès, the western region of Sais Basin, was used as membrane for filtration process [23].

In a posterior work, these two clays will also be tested as membrane support according to their interesting physicochemical properties presented in this work.

2. Materials and methods

2.1. Materials

The area of Sais Basin and especially its eastern part including Fès region has been studied for geological and geomorphological points of view [24-27].The city of Fès is located in the eastern lowest part of the Saiss basin, at an elevation of approximately 400 m above sea level, in the northern part of Morocco, in an area bordered by the mountains of the Rif to the North and those of the Middle Atlas to the South. The deposit is situated in the eastern part of the city of Fès. From a geological point of view (Figure 1), deposit area contains sedimentary rocks of different ages ranging from Triassic to Quaternary, overlying a Palaeozoic impermeable basement complex mainly composed of schists, quartzites marls and limestones.

Samples were extracted in a deposit with detrital facies belonging to upper Miocene. This deposit is the unique where the majority of the local traditional ceramic manufactures use to extract their raw materials.

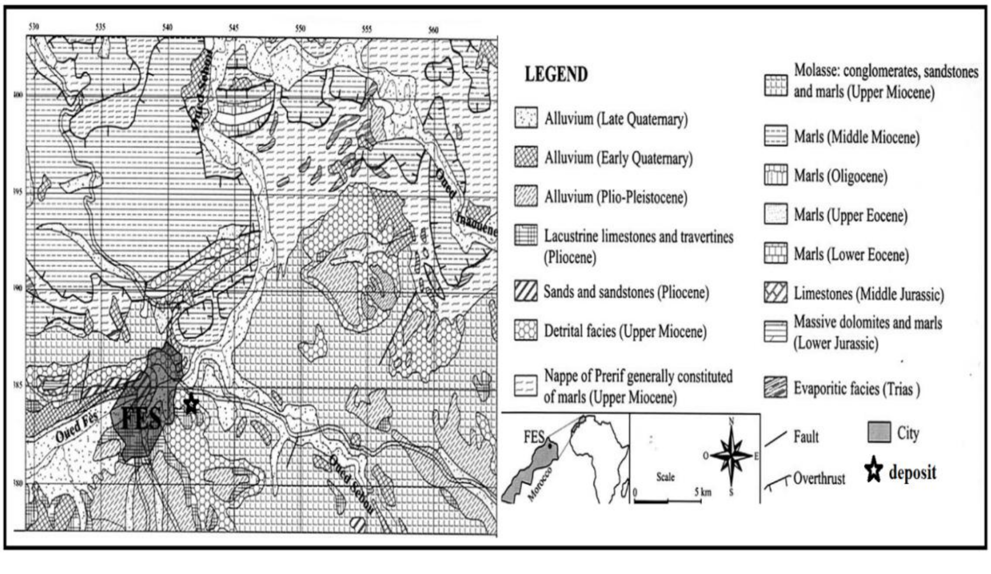

Figure 1: Geological sketch map of the area around Fès city [28].

2.2. Methods

An important quantity of each sample was crushed for homogenization to provide statistically valid samples. Small quantities were dried at 60 °C for 48 h and grounded in an agate mortar for further analysis. Powders were characterized by X-ray diffraction (XRD), particle size distribution, chemical analysis, thermogravimetric analysis (TGA/DTG), and plasticity.

The XRD analysis were carried out using a Philips X'Pert PRO diffractometer operating with CuKα radiations (Kα=1.5418 Å), on the powdered bulk sediment rock and on the powder corresponding to clay fraction (<2 μm) to provide additional information essential for the identification of clay minerals according to the procedure of Moore et al. [30]. For bulk rock analysis, the relative abundance of minerals (including carbonates) was estimated from the height of the main peak. For clay fraction analysis, the whole sediment was decarbonated with HCl (0.1 mol/l) and the (< 2 μm) fraction separated by settling in a water column. Samples were mounted as oriented aggregates on glass slides. The three X-ray patterns were recorded in sequence under air-dried or natural condition, untreated sample (UN), after solvation with ethylene glycol (EG) for 24 h in order to examine the possible presence of swelling minerals (smectites), and heating to 550 °C (H) for 4 h to differentiate chlorite and kaolinite. Semi quantitative analysis was performed with an estimated uncertainty of ±5% [30]. Determination of the percentages of clay minerals was based on the calculation of profile parameters such as line position, intensity peak, integrated area, and full width at half maximum (FWHM).

Grain size distribution has been achieved according to AFNOR standards NF P 94-056 and NF P 94-057, based on Ngoc LAN T's protocol. The analysis was carried in two steps: Granulometry test by wet sieving (NF P 94-056) for fraction with a diameter (Φ) superior to 80 μm and granulometry test by sedimentation method (NF P 94-057), based on Stokes's law, for quantifying fractions of particles of a diameter (Φ) lower than 80 μm.

The chemical composition of samples FS1 and FS2 was determined by X-Ray fluorescence. A sequential spectrometer of X fluorescence based on a scattering of wave length was used. It is equipped with a channel of measure based on only one goniometer covering the complete range of measure of (Be to U). The sample preparation is based on the pearls protocol.

The total organic matter and inorganic carbon amount was determinated by Loss- On-Ignition at 550 °C for 4 h and at 950 °C for 2 h. The total carbonate amount was determinate by Bernad Calcimetry method and confirmed by XRD analysis. The plasticity or limits of Atterberg were achieved on the fraction lower than 400 μm. The Limit of liquidity: WL is determined using Casagrande apparatus (NF P 94-052-1) and Limit of plasticity: WP on rolled sample (NF P 94-051), using the method described by Casagrande [31]. The interval between these two limits of Atterberg defines the extent of the domain of the plasticity (IP plasticity Index= WL-WP). Thermo-gravimetric analysis (TGA/DTG) studies were performed using a thermobalance of VersaTherm type. The temperature was increased from room temperature to 1000 °C at a constant rate of 10 °C/min.

3. Results and discussion

3.1. Characterization of the samples

3.1.1. Particle size distribution

A primarily lecture of the results (Table 1 and Figure 2) shows that the half part of FS1 rock fraction is a Clay (< 2 μm) and with only 1% of sand fraction while FS1 has an important silt fraction with 56% and a sandy fraction equal to 8%. Consequently, this analysis allows classifying these materials as marls.

The results of particle size analysis of the studied samples can be plotted in the ternary diagram of McManus, following the relation between sand, silt, and clay components and their controls over porosity and permeability (Figure 3). The diagram shows that both clayey materials FS1 and FS2 are plotted in the low porosity and low permeability region. FS1 contains the highest amount of clay and lower amount of silt with quasi inexistent sand fraction. FS2 sample is plotted relatively with the lowest clay content, but contains the highest sand and silt content.

Both total organic content values of the samples were very low. The $CaCO_3$ contents were similar for both samples (Table 1).

Table 1: Particle size distribution, consistency limits, total organic content, and $CaCO_3$ content of FS1 and FS2 samples.

Physical properties		FS1	FS2
Particle size distribution (%)	Clay (< 2 µm)	50	36
	Silt (2-80 µm)	49	56
	Sand (> 80 µm)	1	8
Consistency limits (%)	Plastic limit	20	20
	Liquid limit	56	36
	Plasticity index	36	16
Total organic content (wt%)		3	3
Total $CaCO_3$ content (wt%)		13	11

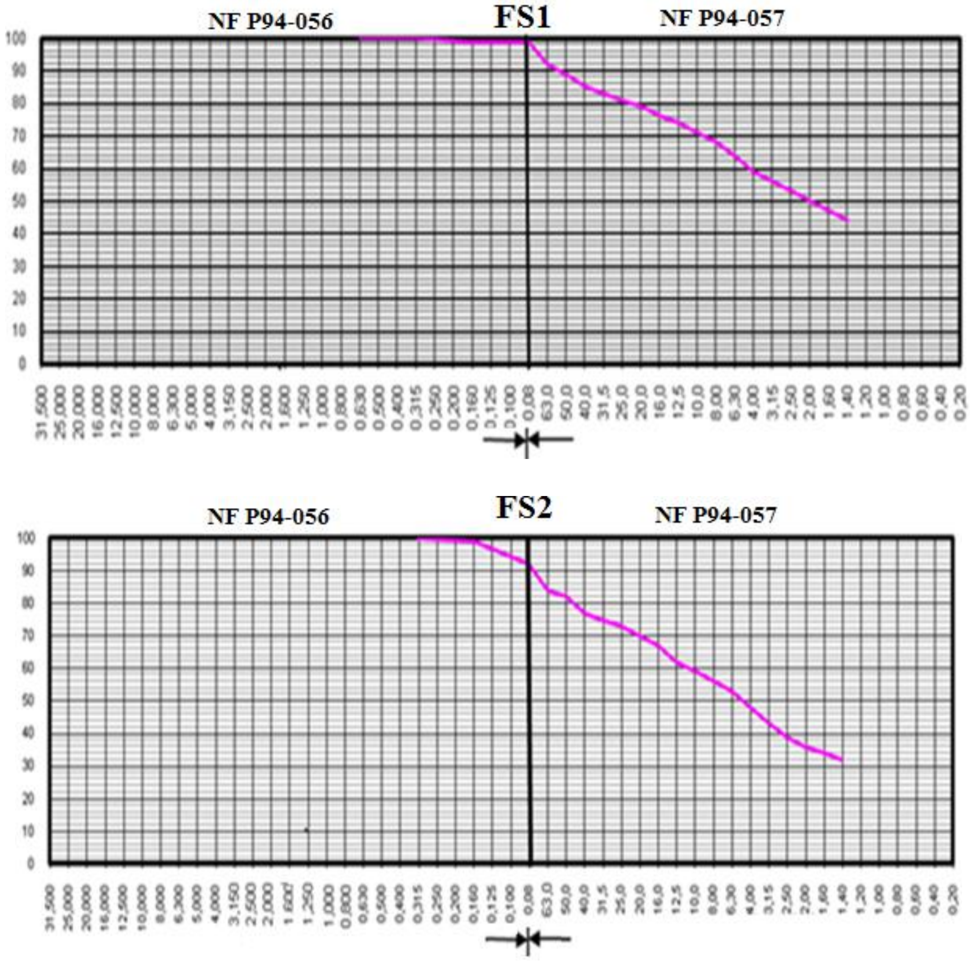

Figure 2: Particle size distribution of the raw clays FS1 and FS2.

3.1.2. Mineral composition

Figure 4.a and Figure 4.b present the untreated XRD patterns of bulk-rock samples collected from Fès. It can be noted that both samples FS1 and FS2 have their major peaks mainly assigned to quartz (Q) (d=4.22 Å and d=3.33 Å) and to calcite (C) (d=3.08 Å). These XRD diagrams do not allow to detect clay minerals and that's why the extraction of this information has been the subject of investigation on oriented aggregates for solving the type of clay minerals and then their respective concentration in the studied rocks.

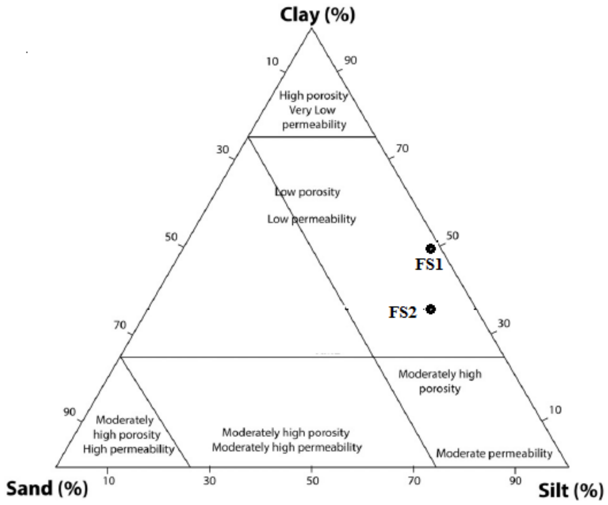

Figure 3: Ternary diagram of studied clay sediments.

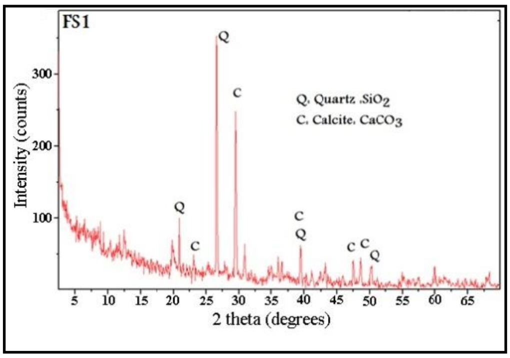

Figure 4.a: X-ray diffraction patterns of raw clay (bulk-rock) FS1.

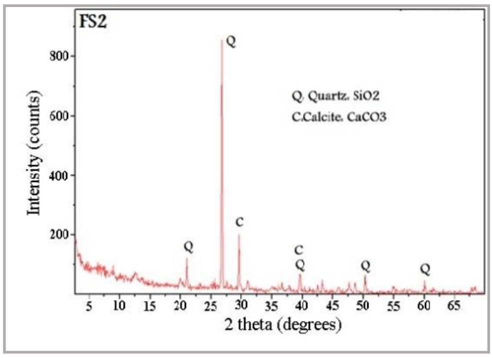

Figure 4.b: X-ray diffraction patterns of raw clay (bulk-rock) FS2.

Figure 5.a and Figure 5.b show the XRD patterns of the (<2 µm) fraction (untreated, glycolated under ethylene glycol, and heated at 550 °C) of the FS1 and FS2 samples collected from Fès.

Qualitative interpretation of XRD diagrams allows the identification of different mineral species by comparison with the available data in the literature [29].

The configuration of both diffractograms of FS1 and FS2 samples is similar. For both samples peaks of illite, smectite, and kaolinite are the relatively dominant ones, while peaks of chlorite and some mixed layers are weak.

In general, smectites have the property to be swelled under ethylene glycol steam [32]. Based on this property, in order to identify the possible presence of swelling minerals, at Figure 5.a and 5.b, for both samples, (ethylene-glycol steam) it is observed that the typical reflection at $d_{100} \approx 14.06$ Å (overlapping with chlorite peak) is shifted to lower 2θ (d≈17.00 Å) indicating the presence of a smectite as swelling mineral.

Since the reflection observed at ~7.10 Å might be attributed to both kaolinite and chlorite, in order to identify these two minerals, two criteria were followed for both diagrams: the first one is the presence of two typical peaks appearing at ~3.58 Å and ~3.53 Å and corresponding respectively to d_{100} peak of the kaolinite and to the d_{003} of the chlorite. The second consideration is the collapsing of both kaolinite typical peaks when heated at 550 °C. These considerations confirm the presence of both kaolinite and chlorite minerals.

Illite mineral is easily recognized and it's characterized by unaltered peaks by ethylene glycol or heating: The intense $d_{001} \approx 9.95$ Å, $d_{003} \approx 3.33$ Å peak (overlapping with quartz) and a weak peak corresponding to $d_{002} \approx 4.98$ Å. A second peak corresponding to d≈4.22 Å and characterizing the quartz is also observed.

The clay mineral composition refers to the relative abundance and identity of the clay minerals present in a clay material. Mineral composition of the Fès clayey materials (Table 2) shows that FS2 sample had the highest content of quartz with 49% against 34% for FS1. Both samples have a comparable amount of smectite (the clay expandable with water), with a value slightly higher in FS1 (18%) than FS2 (15%). The composition of illite, kaolinite and chlorite are similar for both samples.

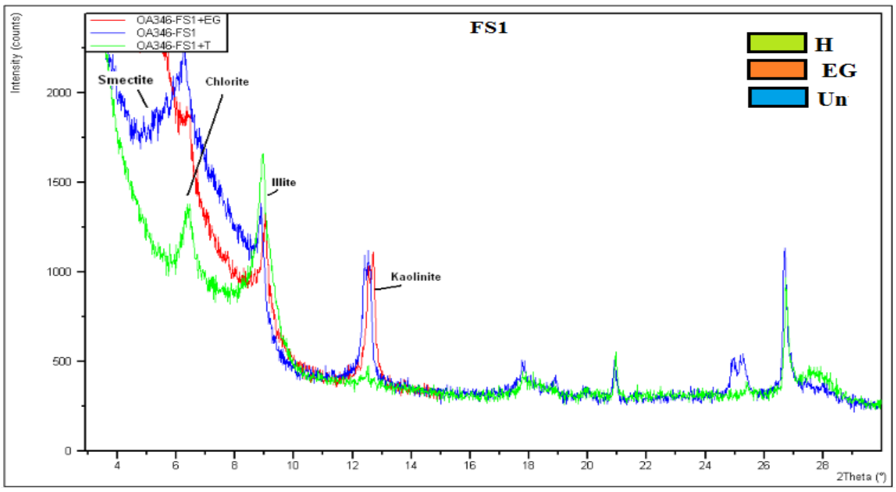

Figure 5.a: Diffractograms of oriented aggregates of FS1: clay fraction (< 2 µm).

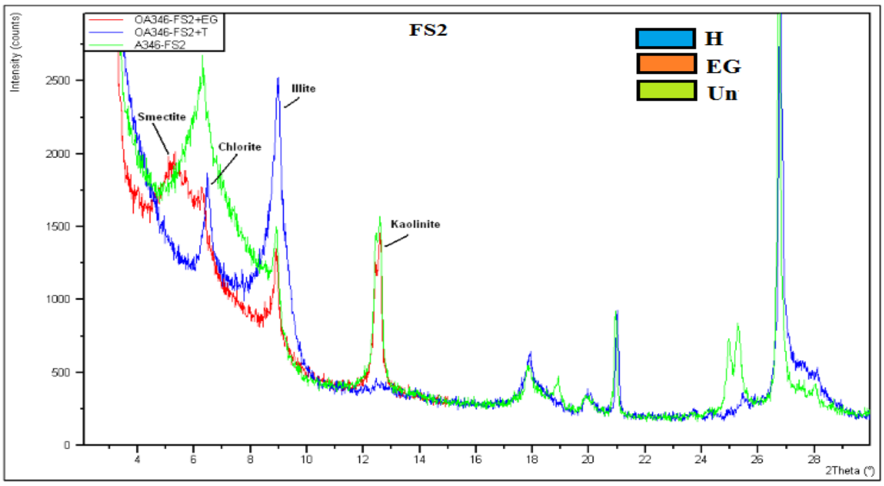

Figure 5.b: Diffractograms of oriented aggregates of FS2: clay fraction (< 2 µm).

Table 2: Mineral composition of the clay samples.

Samples	Illite	Chlorite	Kaolinite	Mixed layers	Smectite	Calcite	Organic matter	Quartz
FS1	10	5	12	5	18	13	3	34
FS2	7	4	9	2	15	11	3	49

3.1.3. Chemical composition

The chemical compositions and the losses on ignition of the FS1 and FS2 samples are listed in Table 3. The analysis shows that the most abundant oxides in both samples are SiO_2, Al_2O_3, CaO and Fe_2O_3 whereas K_2O, MgO, Na_2O, TiO_2 and P_2O_5 are present in small quantities.

The high amounts of CaO for both samples FS1 and FS2 (14.23% and 14.58% respectively) can be mainly attributed to calcite which is present in high concentration in bulk rocks (table 1).

The predominant oxides (SiO_2 and Al_2O_3) are mainly associated with the illite, smectite and kaolinite. The SiO_2 content should be associated with the presence of quartz particles: a highest value for FS2 that present higher sand fraction in particle size distribution analysis and higher quartz content in mineral composition.

In addition, the relatively high SiO_2/Al_2O_3 ratio of both clayey materials is an indication of expressive amount of quartz.

According to Table 3, iron oxide, Fe_2O_3, contents are similar for both samples and around 4 wt%. It is the main colorant in the clayey materials and is a sensitive component to textural aspect of fired clays [33]. Such content confers, to this type of clayey material, a lighter color after firing.

The value of loss of ignition is related to the dehydroxylation of the clay minerals, organic matter oxidation, and decomposition of carbonates and hydroxides [34].

Table 3: Chemical composition of the clays (wt%).

Clays	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	CaO	Na_2O	TiO_2	Lo.I*
FS1	41.28	12.29	4.13	2.80	1.73	14.23	1.02	0.62	20.2
FS2	46.76	10.07	3.97	2.46	1.50	14.58	0.98	0.47	18.2

*** : Loss of ignition**

3.1.4. Plasticity index

In the pottery industry and all the other areas the behavior of the clay in the presence of water is the main process that should be mastered by the manufactures. The plasticity is then the main important parameters of the clay that should be studied. The consistency limits of the samples, which include the plastic limit (PL), liquid limit (LL) and plastic index (PI) (Table 1), are plotted on the Holtz and Kovacs diagram in Figure 6. The diagram shows that FS1 sample is in the highly plastic region, while FS2 belongs to the moderate plastic region in agreement with granolumetric and mineralogical analyses. Effectively, on one hand, these analyses showed, the sandy character and higher amount in quartz for FS2 that are favorable for a lower plasticity but a higher silt fraction that shifts the plasticity to moderate region. On the other hand, a higher amount of clay fraction with a higher amount of smectite for FS1 which are favorable to higher plasticity. It should note that other factors affect the plasticity properties such as origin of geological formation, impurities (non clay minerals), and organic matter [35].

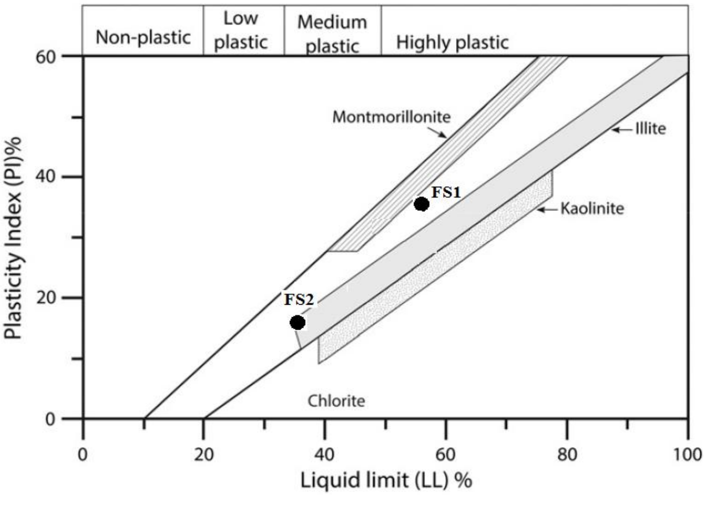

Figure 6: Position of clay samples on the Holtz and Kovacs diagram.

3.1.5. Thermal analysis

The samples FS1 and FS2 were heated in an oxidizing atmosphere, with a heating rate of 10 °C/min. Figure 7 represents the ATG/DTG curves of the samples. It can be seen that the vitrification of both samples occur at higher temperatures (above 1000 °C).

The first DTG peaks, which appeared in both samples at a temperature of about 100 °C, are due to the removal of water physisorbed on the surfaces of particles and to dehydration of interlayer cations of clay minerals. At these temperatures the weight loss was higher in FS2 (5.8%) than for FS1 (5%).

For FS1, a second DTG peak, which is very small and appeared at a temperature of about 400 °C corresponds to the dehydroxylation of structural OH. At this temperature, the weight loss was less than 1%. For FS2 this peak should be seen with slower heating rate.

The third peak, which appeared at a temperature of about 570 °C, is detected for both clayey materials. The weight loss associated with this peak was about 2.5% for FS1 and 2.8% for FS2. This peak probably corresponds to the polymorphic transformation of quartz [36]. This result is in accordance with the particle size distribution, indicating that both samples FS1 and FS2 have largest amount of quartz (table 2).

The last peak was observed at a temperature of about 900 °C with a starting weight loss at 800 °C. This peak is assigned to the decarbonation of calcite [37]. The weight loss corresponding to this region is about 8% for both samples which is an important value in agreement with the calcite amount in FS1 and FS2 rocks (table 1).

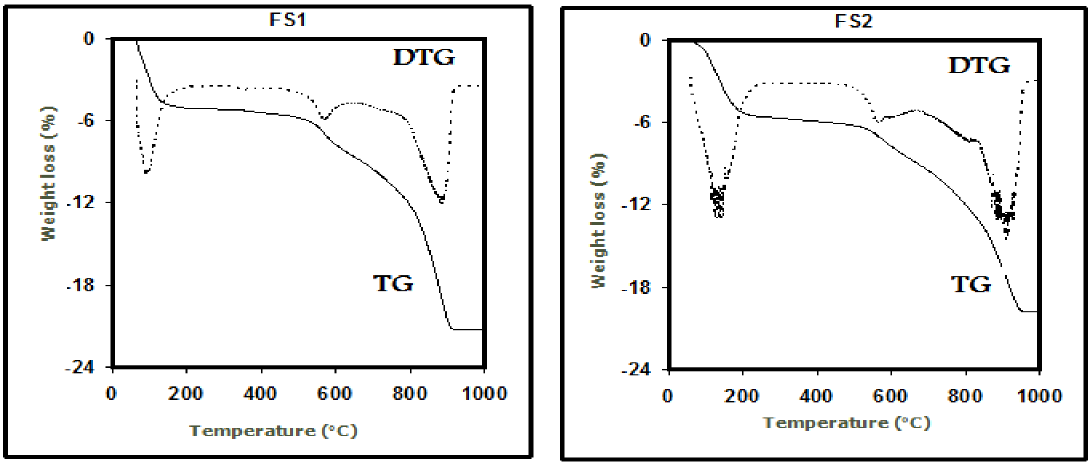

Figure 7: Thermoanalytical curves of FS1 and FS2 samples.

3.2. Suitability for applications

The pottery produced by Fès manufacturers concerns mainly two kinds of products: ornamental products and products based on Zellij. No one of the two raw material is used alone: The first type of products needs raw materials with more sufficient fine particle size amount and less content of agent that decrease shrinkage but reducing cracks to appear, while the second type needs to be cut by metallic tools before the assemblage of the final product. Consequently, there is need for this last type workable matrices containing, in contrary, important quantities of grains with higher particle size provided by the presence of quartz and with less amounts of fine particles. Results of the grain size distribution, plasticity and mineralogy analyses are in accordance with the used formulation by experienced artisans: For decoration and housewares products, the FS1:FS2 ratio of 2:1 is used while the inversed ratio is suitable for the Zellij products. Furthermore, it is obvious that the studied clays are suitable for pottery because of their large content of plastic minerals especially the smectite mineral.

Furthermore, for pottery expectations, extrusion prognostic is possible. Figure 8 presents an extrusion prognostic using the plasticity. The plasticity limit corresponds to the amount of water needed to reach a plastic consistency, which makes it possible for it to be formed by extrusion. The plasticity index is associated with the range between plastic and sludge consistency. For practical purposes, the plasticity index must be above 10%. Clayey materials that present values of PI lower than 10% are not appropriate for building-related ceramic production due to the risk of problems during the extrusion process. The result in Figure 8 reveals that only FS2 is located inside the optimal extrusion region while FS1 sample is located outside both the acceptable and optimum extrusion regions. This suggests that this clayey material is inappropriate for extrusion due to its plasticity Index. The mixture of the two clays is therefore required to avoid such problems.

Additionally, to evaluate the suitability of these raw materials for building products based on granulometric data, we plotted the grain-size weights on the Winkler diagram as shown in Figure 9. It is based on fractions: >20 μm, 2–20 μm and <2 μm.

It can be seen that FS1 sample is plotted in the grain classification III corresponding to roofing tiles and masonry bricks while FS2 sample, belongs to the area IV, suitable for hollow products.

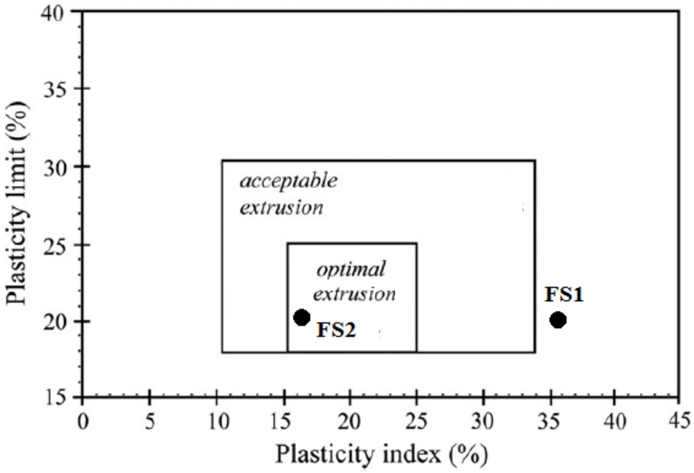

Figure 8: Extrusion prognostic through the Atterberg limits.

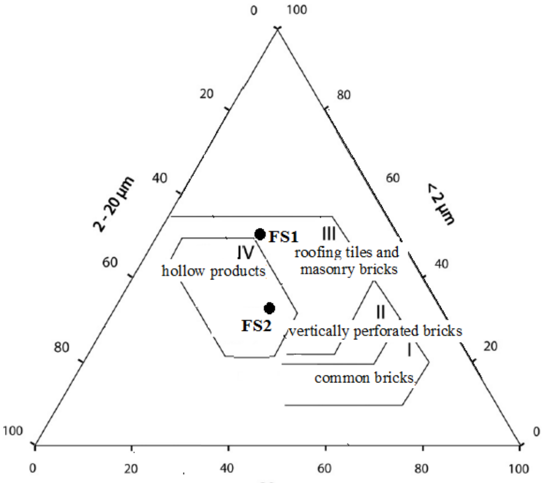

Figure 9: Grain size classification of clay raw materials from Fès in Winkler's diagram.

These applications are possible according to the presence of minerals such as quartz, illite, kaolinite that had a direct impact on ceramic processing. Mineral like illite is well known as a favorable content for sintering step by its contribution to increasing the density when it allows formation of a liquid phase during heating [38]. Quartz facilitates the drying step by decreasing the drying shrinkage and the risk of cracks formation. Quartz also contributes to the glassy phase formation during the sintering step, wherein mullite would be crystallized; the formed glass phase reduces the porosity of the sintered samples.

In Figure 10, the ternary diagram for Fès clayey materials shows that both FS1 and FS2 samples were composed of a mixture of quartz and clay minerals. Based on the criteria of Fiori et al. [39], FS1 sample is most suitable for clay based structural ceramics and FS2 for clay roofing tiles and then there is no need for a special mixture for such applications.

According to all the characterizations of samples FS1 and FS2, one can see that they constitute good candidates for membrane applications. Effectively, mineralogical composition is in favor of a material with good mechanical and chemical resistance. A best porosity for a best permeability can be adjusted by adding adequate porosity agents. The low cost of such material and their abundance remain the best reasons for using them in the filtration process. The development of clay-based inorganic membranes could lead to an important new technological application that would add economic value to the use of the membrane processes in the environment [40].

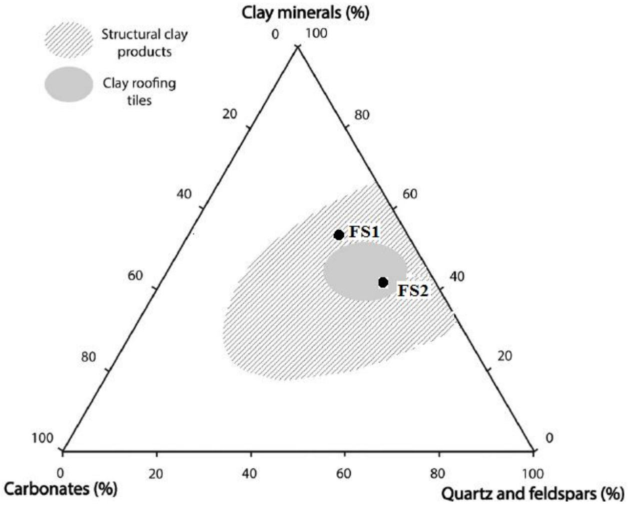

Figure 10: Ternary diagram for the studied clayey materials from Fès.

Conclusion

Particle size distribution analysis allowed to understand the smooth aspect of FS1 sample by the presence of a higher amount of clay fraction (<2µm, 50%), while the grainy aspect of FS2 sample was explained by the presence of a sand fraction (8%) and higher silt fraction (56%). The exploitation of this analysis put both samples among materials with low porosity and low permeability. Total organic content values of the samples were very low, being 3 wt% while the carbonates contents were similar and relatively high: 13 wt% and 11 wt% for FS1 and FS2 respectively.

Mineralogical analysis shows that both samples contain the same minerals: Kaolinite, Illite and smectite as dominant minerals and chlorite with some mixed layers as the minors. This analysis confirms the grainy aspect of FS2 sample and the particle size distribution by the presence of the highest quantity of quartz grains (49% against 34% for FS1). The analysis of the chemical composition shows that the most abundant oxides in both samples are SiO_2, Al_2O_3 CaO and Fe_2O_3 whereas K_2O, MgO, Na_2O, TiO_2 and P_2O_5 are present in small quantities. The high amounts of CaO for both samples FS1 and FS2 (14.23 and 14.58% respectively) is in accordance of the presence of calcite which represents similar concentrations for bulk rocks (13 and 11% for FS1 and FS2 respectively).The relatively high SiO_2/Al_2O_3 ratio of both clayey materials is an indication of expressive amount of quartz in accordance with mineralogical analysis.

The differences in the plasticity of the samples are mainly controlled by the particle size distribution data distribution: FS1 present the highest amount of clay as a raw material and a high plasticity while the FS2 with low clay fraction and the highest sand and silt fractions corresponds to a material with a moderate plasticity.

Both samples present the same thermal behaviour : Dehydration of adsorbed and zeolithic water (0-200°C); dehydroxylation of clay minerals and loss of water of constitution (> 500°C) and decomposition of carbonates above 800°C.

Investigations for suitability of various possible applications show that:

- For local pottery of Fès, the mixtures used as formulations by experienced manufacturers are justified (FS1:FS2 ratio of 2:1 for ornamental and housewares products while the inverse ratio is suitable for Zellij articles).
- In Winkler diagram, FS1 sample belongs to the grain classification that is favorable for its use in roofing tiles and masonry bricks while FS2 sample, belongs to the area suitable for hollow products.
- According to the ternary diagram: carbonates/quartz + feldspars/phyllosilicates, FS1 sample is most suitable for clay based structural ceramics and FS2 for clay roofing tiles and then there is no need for a special mixture for such applications.
- The intrinsic measured characteristics of both clays put them among very promising candidates for membrane technology.

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