

## Engineering Assessment and Applications of Clays, Case Study on Middle Cretaceous (Wasia Formation), Riyadh, KSA

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### Abstract

In this study, our objective is to describe some properties of Wasia Formation clay as raw materials in various ceramic applications. Clays were analyzed by X-ray diffraction, chemical composition and plasticity. The data collected from these techniques show that the kaolinites are major clay phases. The main oxides in the clayey samples are SiO<sub>2</sub> (51-53%), Al<sub>2</sub>O<sub>3</sub> (26.0-28.0%), and Fe<sub>2</sub>O<sub>3</sub> (2.0-3.0%). 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 samples of Wasia Formation. Samples were pressed in a rectangular mould and sintered to a temperature ranging from 850 to 1000°C. Firing characteristics (shrinkage, water absorption, loss of ignition, and mechanical resistance to inflection or bending strength) 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 sample has been determined.

Generally, the chemical and physical properties of investigated clay samples of Wasia Formation indicate their suitability as raw materials for the production of ceramics, Sanitary Ware, Porcelain and Refractories

**Keywords:** Clay; Wasia formation; Ceramic; XRD analysis; Firing

### Introduction

The Clays are one of the oldest raw materials available. They are minerals abundant around the world and, currently, when the societies are more interested in environmentally correct products, clays appear as an important alternative, because they are environmentally-friendly materials. Clays are used as raw materials in many industrial fields (ceramics, paper, paint, petroleum industry, clarification of various effluents, catalysis etc.,) [1,2]. Their applications are tightly dependent upon their structure, composition, and physical attributes. The knowledge of these characteristics can help for best exploitation and eventually may open up new areas of application. Clays are widely used in the manufacture of many traditional ceramics. Kaolinite is the most widely used clay mixture in the ceramic industry [3,4]. A potential source of clay materials for ceramic industry was discovered in the middle Cretaceous sedimentary deposits of Wasia Formation. The clay samples from this region are rich in kaolinite, and widely used as raw materials for red brick by the local ceramic industry [5,6]. In the present study, a detailed characterization of these clays is reported including their possible application in faience ceramics production.

The Wasia Formation is exposed in a discontinuous arc from latitude 20°54'N to 30°00'N, for a distance of about 1500 km and a width of about 50 km [7,8] (Figures 1-2b). The thickness of the Wasia at outcrops increases irregularly but persistently from south (25 to 30 m) to north (about 90 m). The Wasia Formation consists mainly of sandstone and subordinate interbedded shale in the outcrops. The kaolinitic clay facies of the Wasia Formation are exposed intermittently for several hundred kilometers from the Al Jawf area in the north of the Kingdom to the Al Kharj area east of Ar Riyadh.

### Stratigraphic contacts

The contact at the base of the middle Cretaceous Wasia Formation is unconformable, and the formation cuts progressively into the older beds from the south (Al-Rub al-Khali) to the north, latitude 26°03'N and longitude 40°30'E (Wadi al-Atj). Around the area of outcrops,

Wasia Formation overlaps the Biyadh Formation where the contact can be marked by the change in lithology from coarse quartzose sandstone of the Biyadh to ferruginous silty sandstone of the basal part of Wasia Formation [6]. According to Moshrif and Kelling [8], the Shu'aiba Formation occasionally exists between these formations at the outcrops. The top of the Wasia Formation is a major regional unconformity (the pre-Aruma unconformity). The upper surface of the Wasia Formation is a disconformity beneath the Upper Cretaceous Aruma Formation, except to the NE where the surface becomes an angular unconformity [8].

### Materials and Methods

The present study was carried out in order to characterize the most representative clays collected from sedimentary middle Cretaceous (Wasia Formation) that have a distance of about 1500 km and a width of about 50 km (Al Jawf area in the north to the Al Kharj area east of Ar Riyadh.). This outcrop consists of white clay intercalated with sandstone and clay laminations (Figures 2a and 2b).

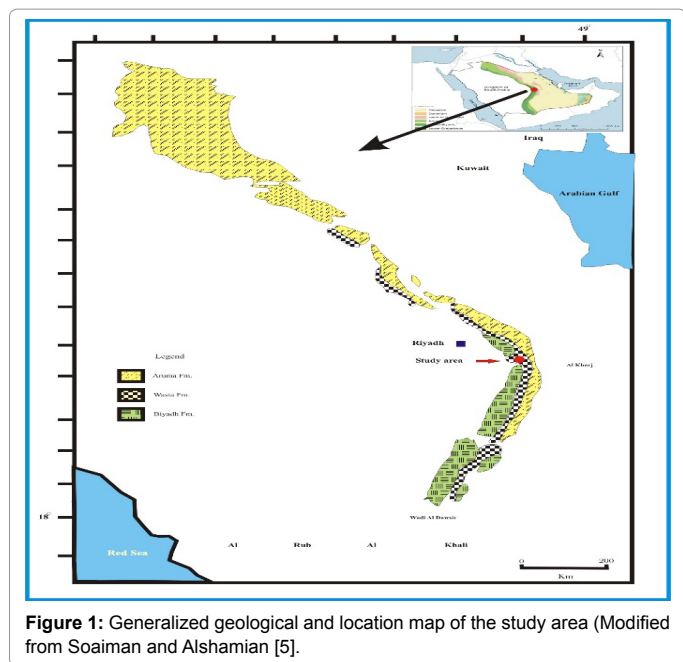
In order to ensure about 3 representative samples, no less than 25 kg of clay was collected from this deposit. After extraction, the clay was initially dried at 110°C for 24 h, and then was manually crushed gently to minimize structural damage to the crystal lattice.

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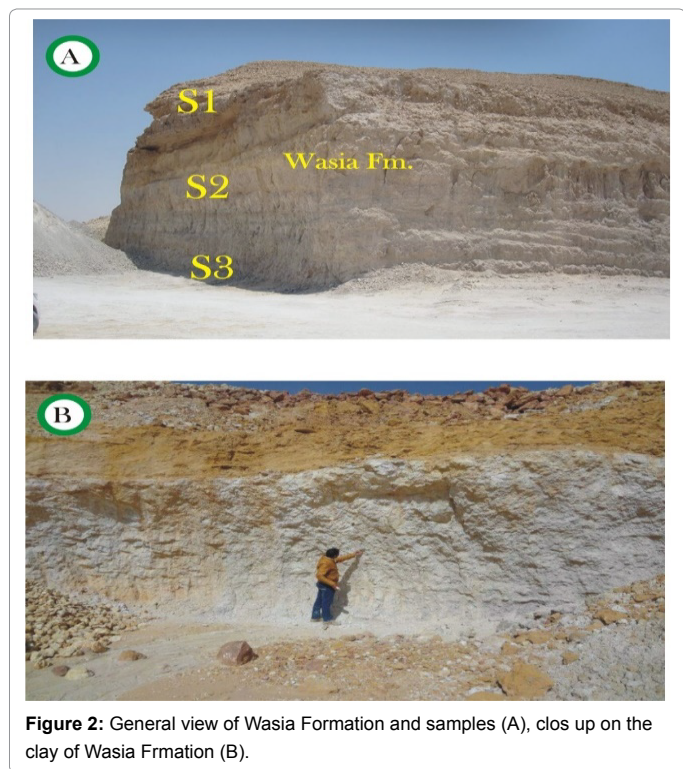
temperature, other were glycolated for 1 h and solvated for detecting expandable minerals, and others heated for 3 h at 550°C to differentiate chlorite and kaolinite. These processes are similar to those described by Thorez [11] and Holtzapffel [12].

### The Physical and Chemical Properties

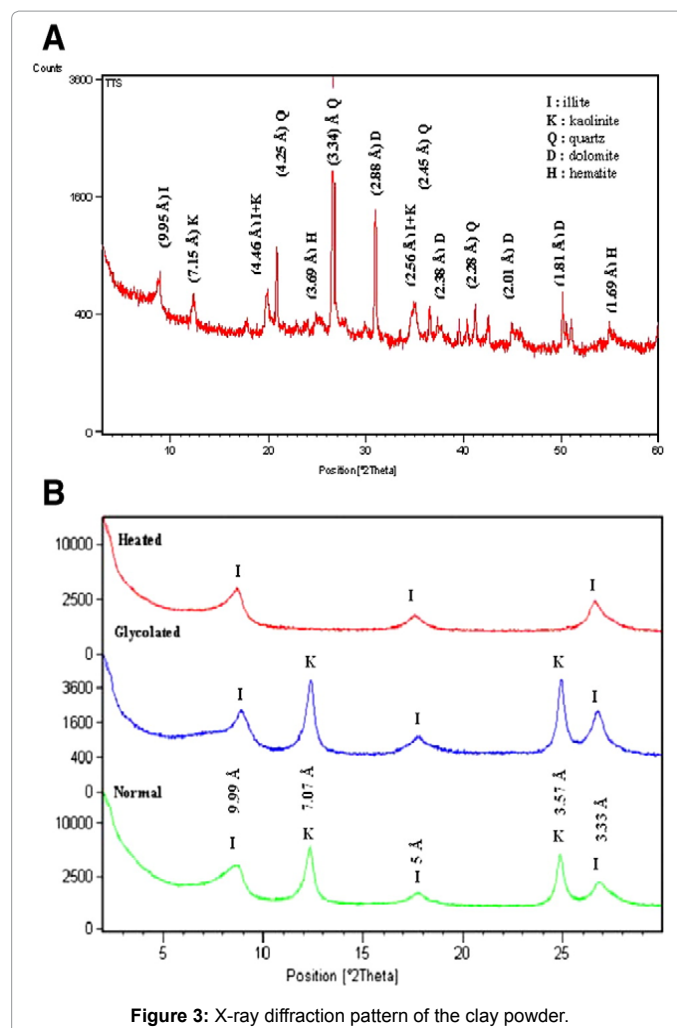
The investigation of physical and chemical properties of kaolin (water absorption, shrinkage and resistance to the inflection as a function of the firing temperature) has led to its extensive use as filler, extender, paper coater, ceramic raw material, pigment, and also it is an important raw material for the refractory, catalyst, cement, and fiber glass industries.

### X-ray diffraction analysis

The following mineralogical phases were identified: illite (ICDD reference pattern: 00-002-0050) as the principal mineral (characteristic peak at 9.79 Å), kaolinite (ICDD reference pattern: 00-001-0527, with peaks at 7.07 Å and 3.55 Å) and quartz (ICDD reference pattern: 01-085-0798, with peaks at 4.22 Å and 3.32 Å). Other secondary mineral phases found in this clay include hematite (ICDD reference pattern: 01-087-1166, peak at 2.69 Å) and dolomite (ICDD reference pattern: 00-036-0426, with a peak at 2.88 Å). Figure 3 shows that the reflections at 7.07 and 3.57 Å disappear after heating to 550°C. This confirms the presence of the kaolinite phase. The peaks at 9.99 Å, 5.00 Å and



The fraction less 2 μm was analyzed on glass slides, according to Moore and Reynolds [9,10]. The fraction 2 μm clay was obtained by centrifuging during 10 min; in addition, each sample was dispersed in distilled water, ultrasonicated to enhance dispersion, and the less 2 μm fraction collected by stake's setting; a small amount of the clay-water suspension was placed by 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



3.33 Å are attributable to illite. The mineralogical composition of raw materials, summarized in Table 1, indicates that the mineral association is the same in all cases and corresponds to the mixture of kaolinite, illite, quartz, dolomite and hematite.

### Chemical analysis

The chemical analyses of the oxide percentages of the studied samples are shown in Table 2, which most abundant oxides in the studied samples are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and Fe<sub>2</sub>O<sub>3</sub>. The results expressed in oxide percentages, confirm the presence of silica (51-53%) from clay minerals, quartz, and feldspar. The alumina (26-28%) comes from clay minerals and feldspar; in and the alkaline elements, mainly potassium oxide associated with illite content for all samples. The alkalis content (K<sub>2</sub>O + Na<sub>2</sub>O) is high (~0.3%) and TiO<sub>2</sub>; 1.46-1.153%. These oxides reduce the refractory temperature of clays [13,14]. The iron oxide content varies between 2% and 3% and it can be considered acceptable which is in agreement with the range used in the literature for ceramic production. This oxide will reflect a uniformity and stability of the tonality of color after firing [15-19]. The chemical and mineralogical analyses of the studied samples are in coincidence with the clays used as ceramic raw materials reported in the literature [20,21]. The CaO + MgO content is suitable (~1.02%) for the clay to be used as a raw material in the manufacture of silico-aluminous refractory products, although the alkali content is acceptable. It is suitable as a filler and earthenware (white ware). It is being quarried for the manufacture of sanitary ware.

### Evaluation of plasticity

The evaluation of plasticity was performed by Atterberg limits method (L.C.P.C, 1987) [10]: 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 [16] and by Grim [17]. The 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.

The suitability of the clay material for ceramic faience products was assessed by determining the Atterberg limits. One may observe that all clays present similar values of plasticity, which according to literature classifies as of medium range (7% < PI < 15%) [2]. The maximum values of the LPL can be observed close to 45.0 wt% (Table 3), which are in agreement with the range defined in the literature (30-60 wt.%) for ceramic production. The Casagrande diagram based on above data (Figure 4) demonstrates that all samples have satisfactory

Samples	Illite	Kaolinite	Quartz	Dolomite	Hematite	Sum.
S1	45	16	24	13	2	100
S2	48	17	22	10	3	100
S3	52	18	20	9	1	100

Table 1: Mineralogy of the Wasia clays' samples estimated by XRD analysis (wt %).

Samples	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	L.O.I
S 1	2.92	53.46	0.99	0.18	0.28	0.12	1.5	0.04	0.3	28.4	11.53
S 2	2.43	51.21	0.87	0.15	0.23	0.15	1.53	0.06	0.33	26.25	12.45
S 3	2.22	52.29	0.95	0.16	0.25	0.13	1.46	0.05	0.31	27.32	11.8

Table 2: Chemical compositions (wt. %) of raw and purified clay raw materials.

Samples	LPL	UPL	PI
S1	45	30	15
S2	43	30.5	12.5
S3	44	28.5	15.5

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

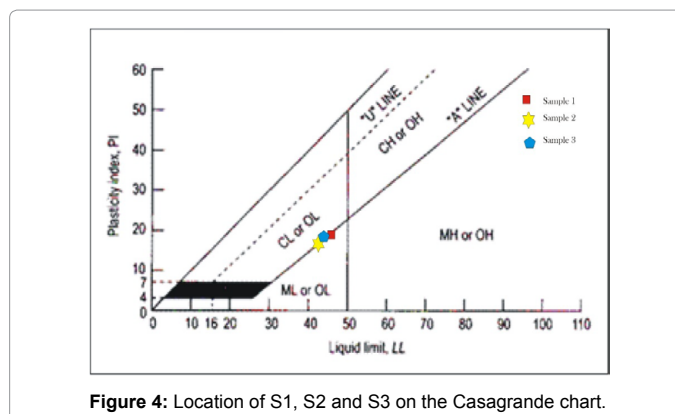


Figure 4: Location of S1, S2 and S3 on the Casagrande chart.

extrudability and a medium plasticity. 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.

### Industrial processing and results

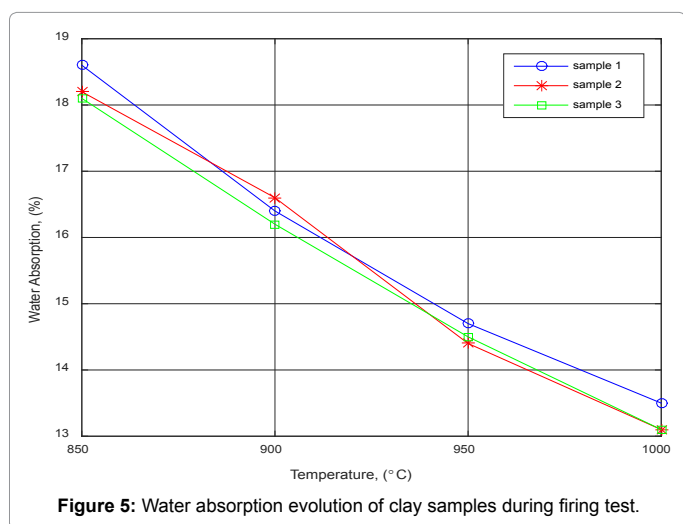
The preparation of clay samples (S1, S2 and S3) and dry grinding in ball mills to pass a 500 µm sieve. The obtained mixture was humidified (6.5 wt% moisture content) and sieved to pass through 1 mm screen in order to obtain suitable powders for pressing. Samples for 100 × 50 × 5 mm were uniaxially pressed 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 constant weight was achieved. The pieces were finally heated to 850, 900, 950 and 1000°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 temperatures are chosen typically for temperatures of industrial ceramic faience. The following industrial applications of the Wasia clay deposits that carried out in the present study:

**The Water absorption:** The water absorption values, determined according to the EN 99 [18] standard, were calculated from weight differences between the as-fired and water saturated samples (immersed in boiling water for 2 h). Water absorption is the parameter which according to EN 100 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 805 to 1000°C the water absorption is nearly (18.6%) (Table 4). 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 1000°C the values of Water absorption decrease, that is associated with a more significant liquid phase formation. This phase



Samples	Temperature C°	Water absorption	Firing shrinkage	Bending strength (N/mm <sup>2</sup> )	LOI (wt.%)
S 1	850	18.6	0.63	10.2	10.1
	900	16.4	1.36	13.7	11.3
	950	14.7	2.56	20.3	12.4
	1000	13.5	3.23	23.5	13.7
S2	850	18.2	0.61	7.4	10.3
	900	16.6	1.41	11.3	12.6
	950	14.4	2.45	14.5	13.5
	1000	13.1	3.41	19.4	14.1
S3	850	18.1	0.6	11.2	9.8
	900	16.2	1.4	14.3	11.4
	950	14.5	2.67	19.3	13.2
	1000	13.1	3.54	22.4	14.2

**Table 4:** Results of the physical parameters according to the temperature of three samples of ceramic faience.



**Figure 5:** Water absorption evolution of clay samples during firing test.

penetrates the pores, closing them and isolating neighboring 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 (Figure 5).

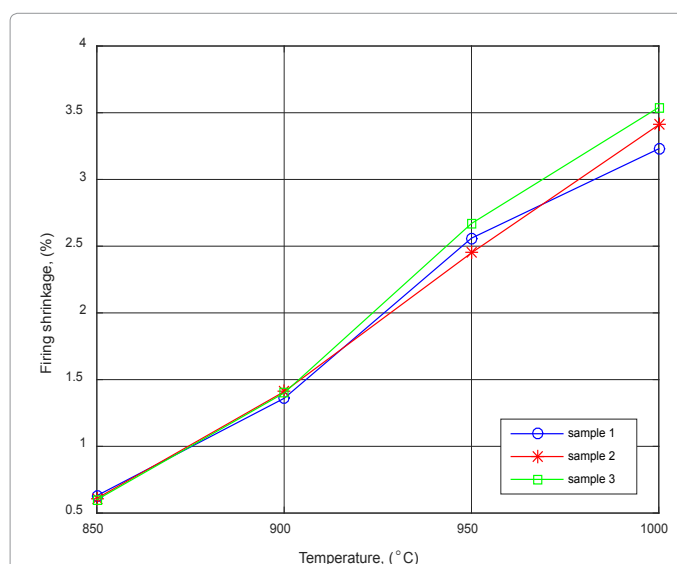
**The firing temperature (Shrinkage Temperature):** The firing temperature is an important factor enhancing the mechanical resistance and durability of end products in ceramic faience, as the material becomes denser. This is also an important engineering quality index for building materials. This effect is due to the progressive formation of calcium silicates and melts phase filling porosity [19], 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. Figure 6 displays an increasing of firing shrinkage with increased firing temperatures for all samples.

The gradual increase of the free CaO content is resulting from the decomposition of dolomite  $\text{CaMg}[\text{CO}_3]$ . The  $\text{CO}_2$  released from the decomposition of carbonate during firing increases porosity of the fired specimen [22]. The free lime reacts with amorphous metakaolinite, which is gradually consumed at increasing firing temperature [19]. The effect of the temperature was to increase the resistance by means of

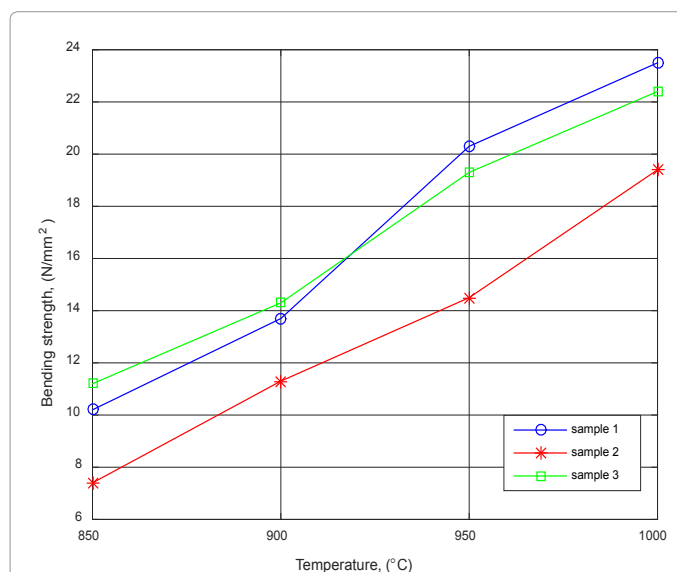
densification. A color is red for all samples, getting darker for increasing temperature due to the high concentration of iron oxides content [10]. Above 950°C, the firing shrinkage ranges from 0.63 to 3.54% (Table 4) in this temperature illite decomposition. The densification behavior of the clay is influenced by the sources of flux materials such as  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$ , which favour the formation of vitreous phase.

**Bending strength ( $\sigma_f$ ):** 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.

The mechanical properties rather straight-forwardly correlate with the other parameters studied. Compressive strength increases as the sample becomes denser as a result of decreasing porosity. This effect is most pronounced above 1000°C, as the densification effect is higher. Figure 7 depicts the variation of bending strength with temperature



**Figure 6:** The firing temperature evolution of clay samples during firing test.



**Figure 7:** The Bending strength evolution of clay samples during firing test.

for the studied clays. 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 [21]. 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. The bending strength ranges from 7.4 to 23.5 N/mm<sup>2</sup> (Figure 7).

**Weight Loss on Ignition (LOI):** The reduction in the weight of each biscuit between drying with 110°C and the various temperatures of cooking is given by the formula:

$$\text{Weight loss on ignition wt:\%} = 100 \frac{(m_{110} - m_T)}{m_{110}}$$

Where;  $m_{110}$  = sample mass at 110 -C;  $m_T$  = mass of specimen fired at temperature T [20].

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 inflexion of the thermally treated samples, it is assumed that as the temperature was increased, the carbonate in clay become deformed into CO<sub>2</sub> [20]. 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 CaCO<sub>3</sub> decomposes to CaO accompanied by the evolution of CO<sub>2</sub> outside the structure of fired bodies. The loss on ignition increases with increasing the fire temperature and ranges from 9.8 to 14.2% (Figure 8). There is no high deference is recorded between the study samples (Table 4).

## Conclusions

Representative raw materials of Wasia Formation of Middle Cretaceous are characterized by chemical and XRD analysis. It appears that the clay used was 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 Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, since they have a decisive influence on the refractoriness and strength of the

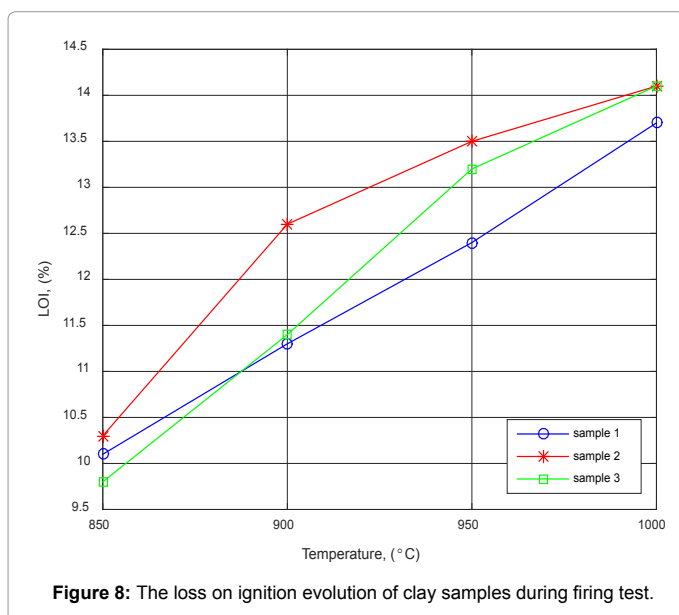


Figure 8: The loss on ignition evolution of clay samples during firing test.

final product. 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 (up to 50 wt.%) content they may possess a refractory behavior. The relationship between water absorption, shrinkage and resistance to the inflexion 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 affirmed 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.

From the investigated characteristics (shrinkage, water absorption, loss of ignition, and mechanical resistance to inflexion or bending strength and chemical aspects) the clay of Wasia Formation are suitable for the manufacture of structural ceramic products, with or without additives depending on the ceramic type and also as raw materials for the production of Sanitary Ware, Porcelain and Refractories.

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