
Characterization and thermal analysis of raw clay for ceramic product design

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Abstract:

Clays (kaolins) are considered as one of the most important raw materials that could be considered as a suitable source for synthesis of both conventional and advanced ceramics. Nowadays, they are still used in the manufacture of ceramic products such as bricks, roofing tiles, porcelain, sanitary wares, wall tiles and floor tiles, and also are used in different industrial chemical processes.

The present work focuses on the mineralogical analysis of clay material samples collected from deposits located in the south of Libya. The raw clay samples were investigated using x-ray fluorescence (XRF) and X-ray diffraction (XRD) as well as thermal analysis (DTA and TG). The results found that, the raw clay samples have different amounts of metal oxides percentage, and the character of the clays is typically kaolin mineral.

Keywords: Clay, Characterization, XRF, XRD, TGA, DTA.

1. Introduction

Clay is a soft white and plastic mineral and has a wide range of applications, in various fields of science, due to the propensity with which they can be chemically and physically

modified to suit practical technological needs. They are used in many applications such as ceramics, medicine, paper coatings, as a food additive, in toothpaste, as a light diffusing material in white incandescent light bulbs, and in cosmetics.¹

Clay minerals are traditionally classified as silicates with layered structure belonging to phyllosilicates group. As an alternative classification, clays belong to hydroxides of silicon, aluminum or magnesium, because content of oxygen in the structure of clays is higher than Al, Si, Fe and Mg. In the past, particle size criteria was taken into consideration as one of the methods to differentiate clay minerals. The layered structure of clay minerals is one of the major properties that allows them to be classified as a separate group of silicates. The basic structure of the layer of clay minerals is defined in terms of sheets composed of octahedral or tetrahedral.

The sheets may be arranged in several ways to create layers with different compositions and chemical properties.²

The tetrahedral sheets are composed of tetrahedral consisting of atoms coordinated to four oxygen atoms. Usually the atoms that are coordinated in the tetrahedral sheet are Si^{4+} , Al^{3+} and Fe^{3+} . The tetrahedral is arranged in the sheets in the form of hexagonal nets, which may be deformed. The distance between free oxygen in a net is close to 0.13 nm and this value is close to the O-O distance of a coordination of octahedron 0.14 nm. Therefore the tetrahedral layer fits almost perfectly on the top of octahedral layer.³

The different arrangements of the sheets in the layers are the decisive factor in classifying the minerals in groups according to their structural features. In accordance with the classification proposed by S. Ismadji *et al*, layers consisting of one tetrahedral sheet and one octahedral sheet are commonly known as TOT structured

minerals, classified as a 1:1 type of structure. On the other hand, minerals ascribed to the group 2:1 are built from the repetition of TOT units, where octahedral sheets are linked with tetrahedral sheets from the apical and bottom part of the sheets.⁴

Kaolin is a natural aluminum silicate hydrate, which is free of most contaminants. Minerals are included in the kaolin is kaolinite, nakrit, decree, and hallosyite ($\text{Al}_2(\text{OH})_4\text{SiO}_5$).⁵

As a representative of the 1:1 layer structure, kaolinite is built by a sequence of layers consisting of tetrahedral sheets and octahedral sheets (Fig. 1). Predominance of Al^{3+} in the octahedral sites of kaolinite and low amount of substitutions by Fe^{3+} or divalent ions like Mg^{2+} is the major reason for a low layer charge, which is close to zero.⁶

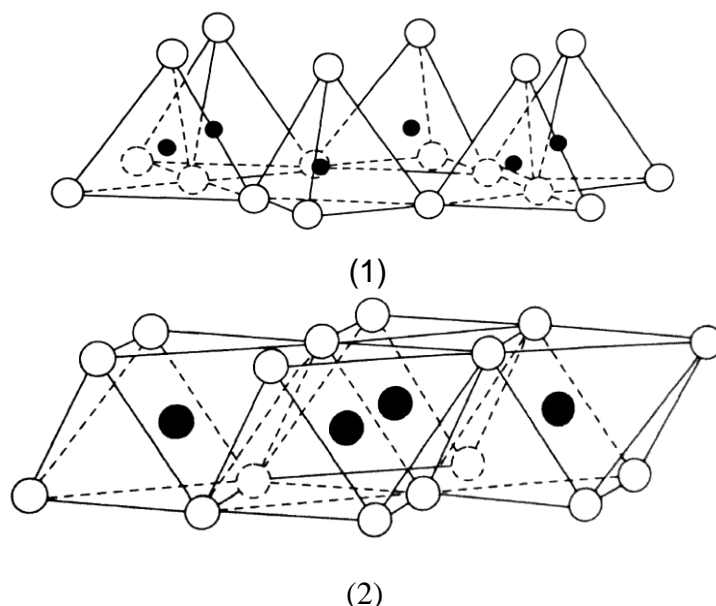


Figure 1. Kaolin (clay) structure: (1) Tetrahedral sheets (2) Octahedral sheets

The kaolinite layer is essentially neutral and two continuous layers are linked by hydrogen bonds $\text{Al}-\text{O}-\text{H}\dots\text{Si}-\text{O}-\text{H}$. The

strength of hydrogen bonds is related to the position and orientation of OH groups in the interlayer space of kaolinite. In kaolinite

primitive cell four OH groups connected with octahedral sheet are distinguished. Three of them are located at the inner surface of the layer and one inside the layer. These inner surfaces OH groups almost perpendicular to the tetrahedral sheet of the next layer to form strong hydrogen bonds. If the OH groups are parallel to the layer, they are not involved in the H-bonding with basal oxygen atoms of the adjacent client layer Akiba.⁷

In this paper the chemical and mineralogical composition of three clay samples selected from the south Libya region were examined. A wide range of techniques was employed, including X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetry (TGA), and X-ray fluorescence.

2. Materials and Experimental

2.1. Raw clay

Based on a previous geological survey carried out by industrial research center (Tripoli).⁸ Three different clay samples from different location for this study were selected at south of Libya. One from Semno area (60 km away from Sebha city), on from Ubari city (Kheraig) (152 km south Sebha

main road) and one from one from Alzegene area (7 km from Semno and 67 km from Sebha city). The tables 1 show selection of some this location based on a previous geological survey.

2.2. Experimental Procedures

The samples were crushing individually by mechanical winning and hand digging. Hand digging was employed in this work based on the ease of the process and the low cost involved. Then grinded in a porcelain ball mill with a porcelain balls as a grinding media until completely passed through standard sieve. They ground clays were then sieved with a sieve of 75µm standard sieve, the remains to the mortar, then re-ground and re-sieved till all the samples have successfully passed through the sieve to reach a particle size less than 75µm.

3. Mineralogical of composition of the investigated of kaolin (clay) sample:

3.1. Chemical composition of raw clay samples

The chemical analyses of the raw material clay were carried out by X-ray fluorescence (Table 6). The mineralogical compositions were identified by (BRUKER-XRF-3400) ray powder diffractometer.

Table (1): Location of the selected clay batches

Bach no	Location
1	Semno (60 km away from Sebha city)
2	Ubari (Kheraig) (152 km south of Sebha main road 52 km from Ubari city)
3	Elzegene (7 km from Semno and 67 km from Sebha city)

Table (6) chemical composition of clay samples (XRF)

Componte (%)	Semno clay (sample 1)	Kheraig clay (Sample 2)	Elzegene clay (sample 7)
SiO ₂	58.10	48.70	57.86
TiO ₂	1.81	1.25	2.20
Al ₂ O ₃	30.01	35.18	29.20
Fe ₂ O ₃	1.40	2.00	1.87
MnO	0.01	0.02	0.02
MgO	<0.01	<0.01	0.03
CaO	0.05	0.13	0.24
Na ₂ O	<0.01	<0.01	<0.01
K ₂ O	0.26	0.84	1.12
P ₂ O ₅	0.06	0.10	0.06
Cl	<0.01	<0.01	<0.01
SO ₃	<0.01	<0.01	<0.01
Sr	0.022	0.055	0.023
L.O.I	7.96	11.39	7.24

The results of the chemical analyses described earlier indicate that the three investigated samples are composed mainly of ≈ 48 -58% silica (SiO₂) and ≈ 29 -35% alumina oxide in addition to little contents of other impurities namely; Titania (TiO₂), ferric oxide (Fe₂O₃), calcium oxide (CaO), magnesia oxide (MgO), sodium oxide (Na₂O), phosphorus pentoxide (P₂O₅) as well as potassium oxide (K₂O). Sulfur trioxide (SO₃), chlorine (Cl) and strontium (Sr) showing low percentages below the levels. These oxides constitute ≈ 82 -86% percentages of each clay. It is noticed also that the samples possess ≈ 7 -19% loss on ignition (L.O.I) which confirms that the samples are mainly kaolinite Al₂O₃.2SiO₂.2H₂O where the loss on ignition corresponds to the loss of chemically combined water the lattice of kaolinite mineral.⁹

The table indicates that samples 1, 2 and 3 selected from Semno, Kheraig and Elzegene respectively contain relatively higher proportions of Al₂O₃ and SiO₂, and through the results of previous tests, all samples contain a comparable ratio of oxides and a high proportion of silica oxide and aluminum oxide in the clay samples will be the most suitable for high ceramic preparation.¹⁰

3.2. X-ray diffraction analysis (XRD):

The X-ray diffraction technique (BRUKER-XRD D5000) was used for the mineralogical composition of seven raw clay samples. Figs. (2-7) show the x-ray diffraction of the seven raw clay samples used as starting materials in this investigation. The figures show the following results:

(a) Samples (1) (Figs. 2) selected from Semno location show only the main peaks characterizing kaolinite minerals with high

intensities at 2θ : 12.5, 13.5, 21, 21.5, 23, 23.5, 25, 26.5, 38.5, 39 and 39.5. Also, the figures show the main peak characterizing quartz mineral (SiO_2) could be detected at 2θ : 26.8. It could be recognized that the intensity of the main peak characterizing quartz mineral is maximum in Semno clay (Fig. 2). Some peaks characterizing muscovite, montmorillonite and with relatively lower intensities, few peaks with very low intensities characterizing illite ($(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$) could also be detected in Semno clay at 2θ : 17.8, 19.9, 30.9 and 34.5.

(b) Samples (2), (Fig.3) all main peaks characterizing quartz mineral were detected with relatively high intensities. Only few

peaks characterizing kaolinite with low intensities, and few peaks with very low intensities characterizing illite ($(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$) could also be detected at 2θ : 9, 16, 20, 27, 30, 35, 38.8 and 61,8.

(e) Sample (3), (Fig. 4) show all of the main peaks characterizing quartz with high intensities in addition to the peaks with relatively lower intensities characterizing illite

($(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$) and montmorillonite ($(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})$) minerals, only few characterizing kaolin with low intensities.

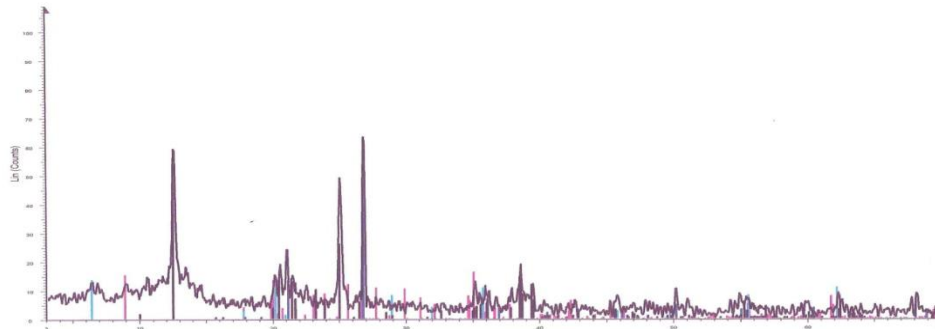


Fig. (2): XRD Patterns sample (1)

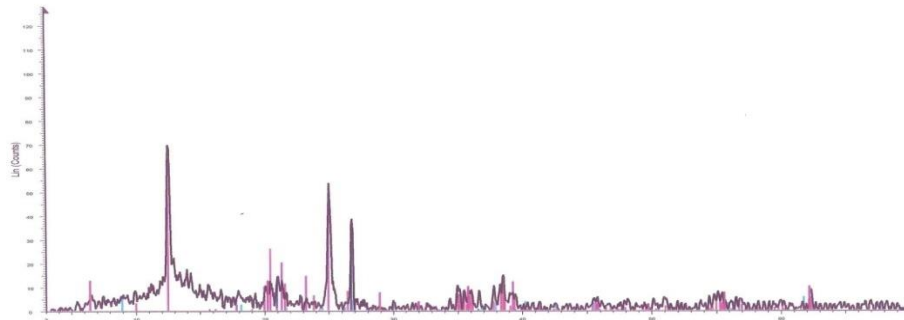


Fig. (3): XRD Patterns sample (2)

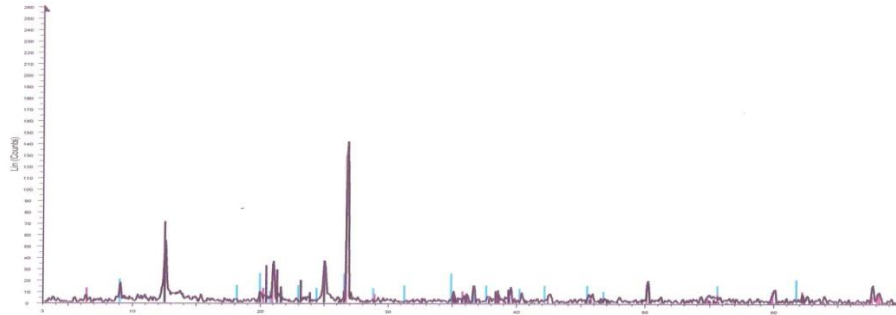


Fig. (4): XRD Patterns sample (3)

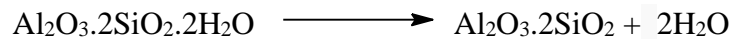
3.3. Differential Thermal Analysis (DTA) and (TG)

(a) Differential Thermal Analysis (DTA)

Differential thermal analysis (Perkin Elmer Analysis) is presented for a large number of clay minerals and related silicates. The characteristics of the thermal curves of illites, kaolinites, and montmorillonites, and other clay minerals are discussed. Thermal analysis diagrams of tree investigated clay samples are shown in

Figs (5 -7). All the figures show two endothermic peaks at $\approx 50^\circ\text{C}$ to 80°C and $\approx 500^\circ\text{C}$. The results show that;

The first endothermic peaks due to evaporation of physically adsorbed water and the second endothermic peak at $\approx 500^\circ\text{C}$ can be attributed to the elimination of constitution water resulting from the loss of hydroxyl groups from the clay structure (dehydroxylation of kaolinite) according to the following equation:



This behavior is the ideal behavior kaolin.^{11, 12}

This confirms the results of X-ray diffraction analysis, which indicate that the seven investigated clay samples used as starting materials in this investigation are composed mainly of kaolinite minerals. The

exothermic peak is found to be at the temperature nearly $980\text{-}10000^\circ\text{C}$. This basically happens due to conversion of meta-kaolin into a spinel phase ($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$), which is finally converted into mullite.

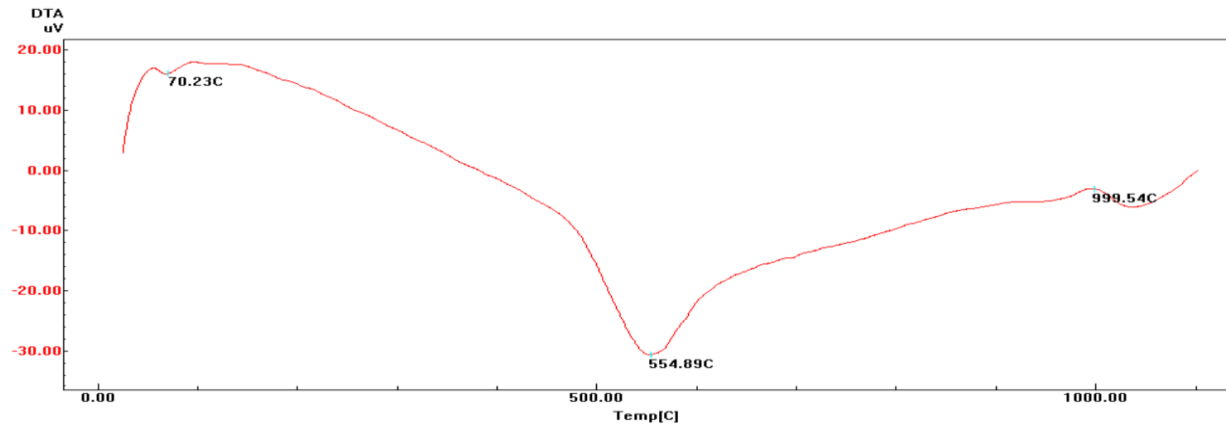


Fig.(5) DTA of clay sample (1)

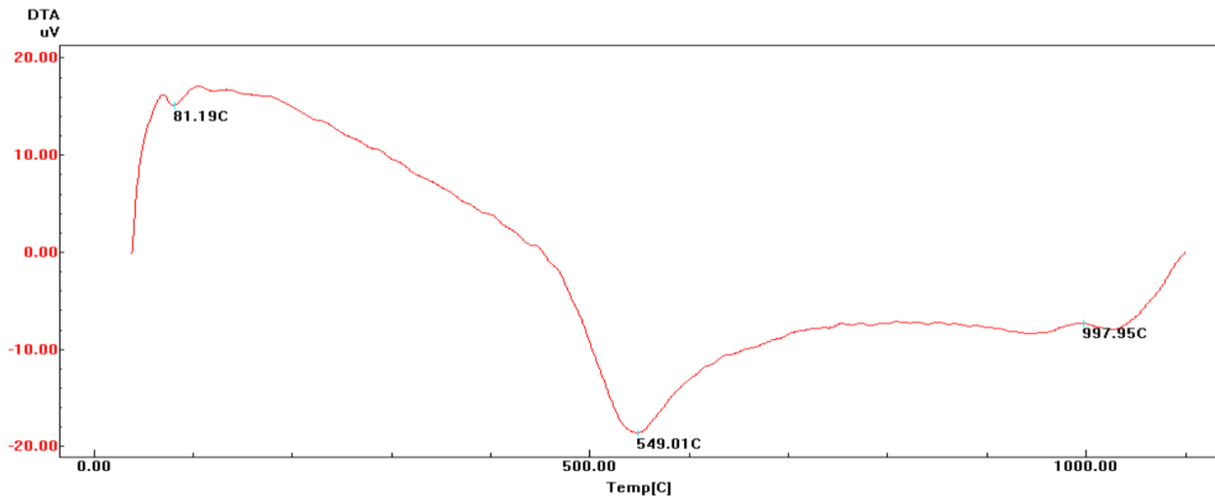


Fig.(6) DTA of clay sample (2)

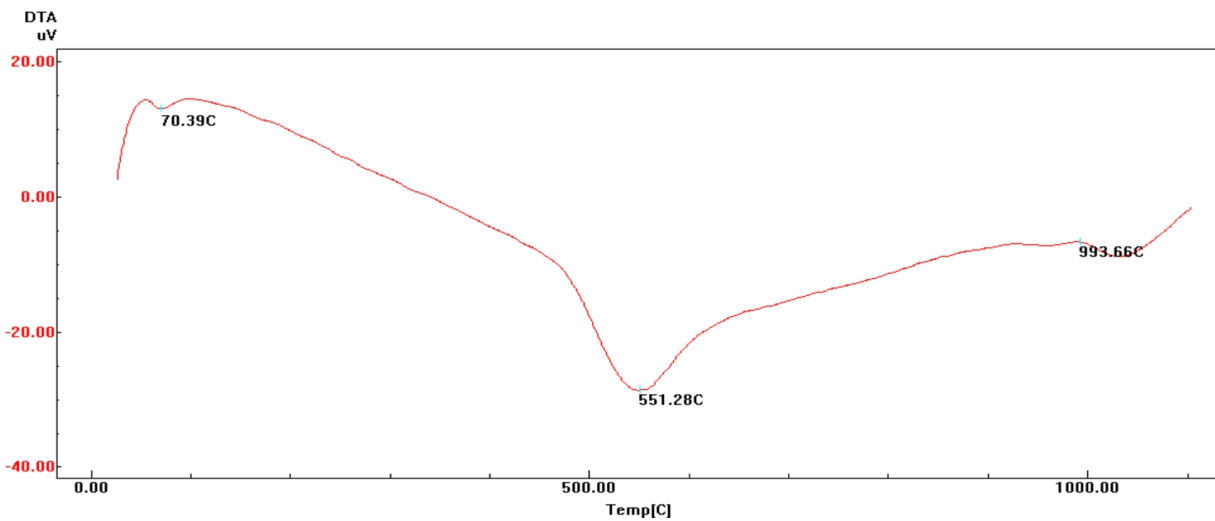


Fig.(7) DTA of clay sample (3)

(b) Thermal analysis (TGA)

Both DTA and TGA characterizations are carried out simultaneously with the same device.

The TG curves of seven clay samples from different location at different depths are shown in Figs. (8-10). The weight loss percentage resulted in the thermal reactions between the sample sherds and the reference material during their firing from room temperature to 1000 °C.

The TG curves of the shreds showed a gradual weight loss due to dehydration of water molecules in the temperature range 50-1000 °C.

In differential thermal analysis, *exo/endo* thermic peaks appearing in all the specimens at different temperature intervals are described as follows: All samples show ideal behavior analysis of kaolin, a considerable percent of weight loss is observed on TG digrams at a temperature range ≈ 500 °C to

550 °C, corresponded with an endothermic peak on DTA diagrams at the same range of temperature. The endothermic peak at 500°C can be attributed to the elimination of constitution water resulting from the loss of hydroxyl groups from the clay structure (dehydroxylation of kaolinite).¹⁴ Previous analyzes have shown (DTA) the next change will take place at ≈ 935 °C – 999 °C when meta kaolinite suddenly crystallizes into the spinel structure or a Si-containing γ -Al₂O₃ and amorphous silica oriented in the same way as the original kaolinite with rejection of silica. It is also observed that the percent of weight loss on TG digrams are larger in samples composed mainly of pure kaolinite or kaolinite with some impurities of quartz (SiO₂), illite (K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,(H₂O)], montmorillonite (Na,Ca)_{0.33}(Al,Mg)₂(Si₄O₁₀) and muscovite KAl₂(AlSi₃)O₁₀(OH)₂.

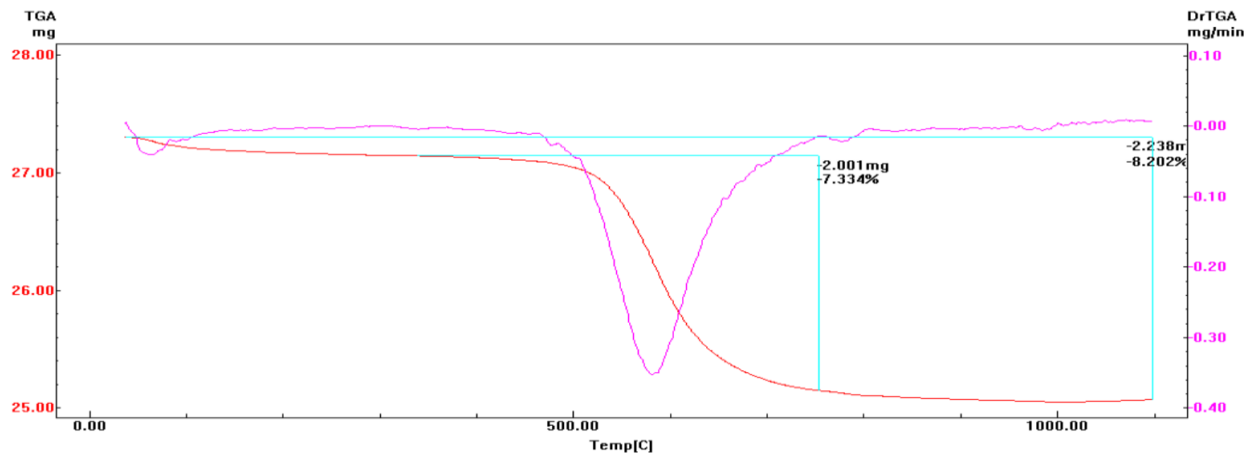


Fig. (8) TGA of clay sample (1)

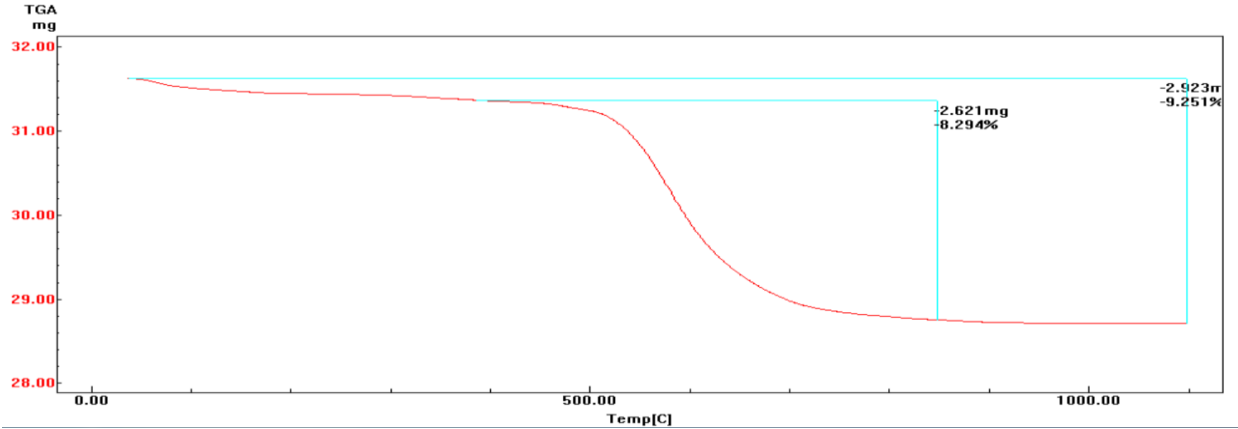


Fig. (9) TGA of clay sample (2)

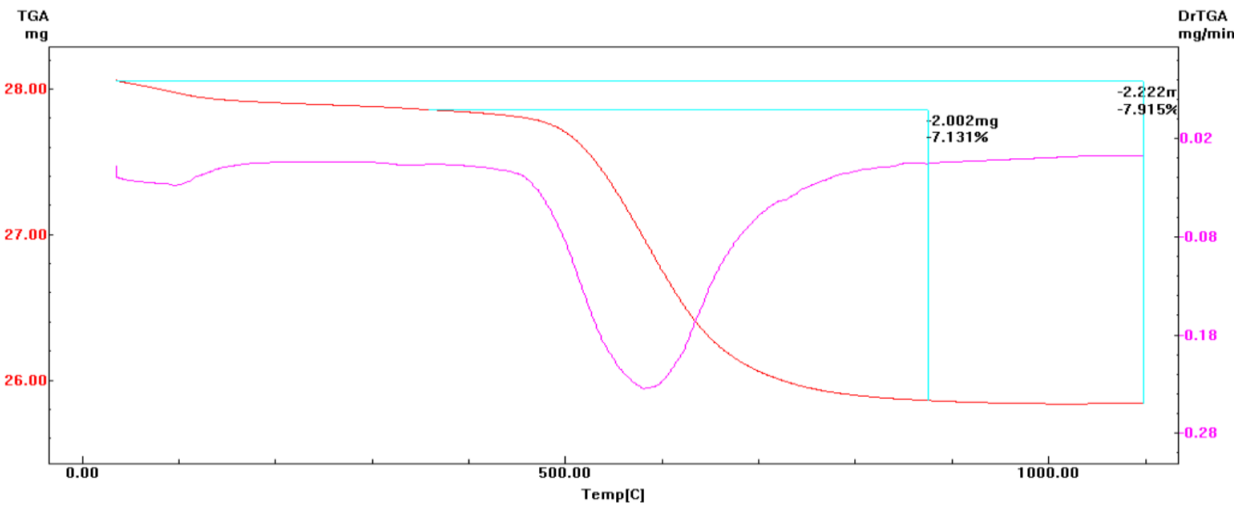


Fig. (10) TGA of clay sample (3)

CONCLUSIONS

Different techniques have been used to characterize raw clay and activated.

The three different clay samples were characterized by X-ray diffraction, X-ray fluorescence, thermal analysis using TG curves, and exothermic and endothermic peaks appeared in DTA curves.

In the XRF analysis, the chemical compounds present in the clay and their concentrations were obtained with the major elements present are expressed in the form of their oxides. The chemical analysis of raw clay shows that the major elements are SiO₂ and Al₂O₃, which are both associated with

the kaolinite structure.¹⁵The ratio of SiO₂ increase in activated sample: this increase is due to the formation of amorphous silica during activation.

On the other hand, thermal analysis of clay samples reveals the percentage of mass loss due to dehydration, dehydroxylation, and the combustion of organic material contained in the clay used to make the ceramics sample studied in the present investigation. The amount of residual mass is mainly controlled by transformation of minerals, dehydration, the amount of combustible material mainly organic materials present and temperature.

The mineralogical studies indicated that the clays have kaolinite as the main mineral phase, and illite, quartz, and montmorillonite as impurities. XRD analysis also indicated the

presence of a small amount of tubular halloysite. In general, the analyzed clays have various minerals, the TG/DTA and curves suggest that the character of these clays is predominantly kaolinitic

التوصيف والتحليل الحراري لبعض عينات الطين المحلي لصناعة وتطوير السيراميك

صالح احضيري المقداد علي عادل احمد ناحي خليل صالح صالح

المخلص: يعتبر الكاولين (الطين) من المواد المهمة في صناعة السيراميك التقليدي والمتطور. في الوقت الحاضر لا يزال الطين يستخدم في صناعة المنتجات الخزفية مثل أطوب القرميد الخزف اللادوات الصحية بلاط الجدران وبلاط الارضيات وايضا يستخدم في العمليات الكيميائية المختلفة. ركزت الدراسات الحديثة على انتاج وتطوير منتجات سيراميكية حديثة ومتقدمة باستخدام الطين مع اكاسيد المعادن مختلفة لتطوير خواص السيراميك المنتج. تهدف هذه الدراسة على التحليل التركيبي المعدني على عينات من الطين المحلي منخوذة من بعض المناطق في الجنوب الليبي. ولقد استخدمت في هذه الدراسة بعض من الاجهزة المهمة للتعرف على التركيب المعدني لعينات الطين, وهذه الاجهزة هي: (XRD) مطياف الاشعة السينية, فلورية الاشعة السينية, وأيضا التحليل الحراري. اظهرت النتائج التحليلية باستخدام الاجهزة السابقة على عينات الطين الداخلة في الدراسة تحتوي على نسبة من اكاسيد معادن مختلفة, من هذه الدراسة يتضح ان معظم عينات الطين الداخلة في الدراسة تحتوي على معدن الكاولين.

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