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Evaluation of the technical potential for developing some Egyptian shales use in the vitrified clay pipes manufacturing

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Abstract

This study was established to investigate the visibility of using many deposits of local shale raw materials for vitrified clay pipes manufacture. Ten composite shale samples were selected from different localities in Egypt. The technological characteristics indicate the suitability of using raw materials from some localities in the studied area for manufacturing the sewer pipes. The characteristics of the fired samples at 1200°C which are; linear shrinkage, water absorption, bulk density, modulus of rapture apparent porosity and chemical resistance are determined and concluded that some of these raw materials are suitable for manufacturing vitrified clay pipes. Each of the Heiz, Gabal Hamza and Monkar El-Wahsh shale deposits have a specific application in the vitrified clay pipes industry, indicating the prominent potential of Egyptian shales to characterize industrial materials.

Key words: Clays, shales, vitrified, pipes, Egypt.

Introduction

Clays and clay minerals are important in geology, agriculture, construction, engineering, process industries, and environmental application. For this reason, particular attention should be given to the exploitation of raw materials in Egypt for industrial application. The present paper aims at investigating a particular application of local shales collected from different localities in Egypt to evaluate their potential for vitrified clay pipes.

Shales have traditionally been used for manufacturing of vitrified clay pipes (VCP). The characterization of shales from the physical, chemical, and thermal standpoint in technical stages is a necessary step. Ten composite samples were collected representing the shales and clays from Qasr El-Sagha, Heiz, Monkar El-Wahsh, Wadi Natrun, Sebaya, Arish, Gabal Hamza, Aswan and two samples from Bahariya Oasis (Fig.1).

Use potentialities of some shale from Egypt in the vitrified clay pipes (VCP). In order to point out the different parameters, which are conditioning the behavior of the raw materials and their suitability for sewer pipes industry, many tests were done on the collected raw materials and fired product. The mineralogical constituents, chemical composition, grain size analysis, thermal analysis were used to evaluate the suitability of these materials in VCP industry. The scanning Electron Microscope and the technological characteristics were used to detect the texture of the ceramic body. The various characteristics of the final product show that some samples are compatible with the international specifications.

In this paper, vitrified clay pipes are prepared from some Egyptian shale in the manufacturing industry and in the Sweillem Vitrified Clay Pipes (SVCP) plant, and the crystalline phases, microstructure of the materials have been studied.

Methodology and study techniques

The mineralogical constituents was determined by X-ray diffraction analysis that carried out on clay fraction less than 2µ in diameter using Philips PW 1140/90 X-ray apparatus cu-k alpha radiation, nickel filter.

The Chemical analyses of composite shale samples were carried out to determine the type and percentage of the major oxides present in the examined samples using X-ray fluorescence (XRF).

The particle size distribution of raw materials influences their behavior during the technological process and affects many properties of clay ceramic products. In natural clay materials, it is difficult to determine how far changes in ceramic properties arise from particle size as much independently of the change in mineral constituents (**Folk, 1954**). However, it is widely accepted that fineness increases plasticity and subsequently firing shrinkage.

On the other hand, the increases in sand size content reduce firing shrinkage and increases porosity (**Sacmi, 2002**). But in general the important requirement of shales and clays which are suitable for producing of sewer pipes is the weight percent of grains above 63 microns 3% maximum. The particle size distribution of the analyzed samples obtained by using a screen analysis is presented in Table 1.

Differential thermal analysis was used to identify the clay minerals and recrystallization during firing is using Netzsch Geratebau Dilatometer 402 EP Germany. The DTA thermograms are very important in all types of ceramic industry because the rate of firing curve changes according to the points of decomposition and the points of loss in ignition to avoid the cracks and collapse of products (**Grimshaw, 1971** and **Handle, 2007**).

Specimens of 80 grams each were molded by using semi-dry pressing by 100 bars; they were of rectangular shape of 131*20mm and approximately 10mm thickness. The samples were fired in kiln at a temperature of 1200°C and soaking time 2hours). Physical and mechanical properties of tested samples namely linear shrinkage, porosity, water absorption, bulk density, apparent porosity, modulus of rapture and chemical resistance are established (**Rao, 1963**).

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The texture of briquettes fired at 1200°C was showed by Scanning Electron Microscope using SEM Model Quanta 250 FEG (Field Emission Gun) with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolution for Gun.1n. FEI Company, Netherlands. It includes photomicrographs of various sites of the sample and with various magnification powers.

Experimental results and discussion

1. Particle size distribution

The grain size distribution of shale samples (Table 1) shows that all samples were confirmed in manufacturing of sewer pipes except two samples which they have high percentage of size more than 63 microns. These two samples are Qasr El-Sagha (9.35%) and Mendishia (6.5%) where the maximum accepted percent is 3%.

2. Mineralogical constituents

The mineralogical analyses are in accordance with the chemical analyses. White shales of the Heiz Formation are very plastic and can be interesting in the manufacturing of VCP, which can be confirmed by industrial tests.

The mineralogical constituents of the studied samples show that the samples of Heiz, Monkar El-Wahsh and Gabal Hamza have kaolinite and traces of dolomite and calcite. These minerals were suitable for VCP industry and the other shale samples have the previous minerals in addition to montmorillonite and halite minerals that unsuitable for VCP industry. The results of XRD study detected phases in the different fired shale samples are mullite, cristoballite and quartz as a major components and hematite, albite as a minor phase in the all tested fired samples.

3. Chemical composition

The results of the chemical analyses related to the major elements, the total dissolved solids (TDS) and the loss on ignition are presented in Table 2. The chemical composition of shales and clays varies within broad limits this due to the fact that the same oxide may be present in several mineral phases that show opposite influences on the products. As a consequence, two clays with similar compositions may show a different technological behavior, according to the particular mineral components.

The chemical composition of the studied shale samples were done and compared to the requirements of SVCP Co. (SiO_2 45: 60%; Al_2O_3 15: 25%; iron oxide 0: 15%; CaO + MgO 0: 10%; Na_2O + K_2O 1: 5%; and TDS 0: 5%). The shale samples of Monkar El-Wahsh, Heiz, Gabal Hamza, Bahariya, Qasr El-Sagha, Aswan and Arish were matched with the previous standard (Table 2).

4. Thermal characterization

4.1. Differential Thermal Analysis (DTA)

Kaolinite starts to lose the moisture exhibiting an endothermic peak at 70-110°C in all shale samples. The decomposition of kaolinite starts at 526-588°C with an endothermic peaks in the studied shale samples to form metakaolinite. The small exothermic peak starting from 940°C shows primary mullite formation.

The endothermic peak at 283.19°C in Sebaya shale sample and at 333.2°C in Aswan shale sample shows the evidence of carbonaceous material. The small exothermic peak at 921°C shows the montmorillonite or glauconite in Qasr El-Sagha and Sebaya shale samples. The small endothermic peak at 731.41°C in Arish shale sample shows the montmorillonite (Figs. 2 & 3).

4.2. Chemical reactions of clays and shales

When clays and shales heated to 1100^{o}C, kaolinite decomposed by first order kinetics according to the following sequence of steps:-

This means that the reaction rate is proportional to the concentration of the substances reacting.

$$\underset{\text{Kaolinite}}{2SiO_2.Al_2O_3.2H_2O} \xrightarrow{500\ ^{o}C} \underset{\text{metakaolinite}}{2SiO_2.Al_2O_3} + 2H_2O$$

$$\underset{\text{Metakaolinite}}{2SiO_2.Al_2O_3} \xrightarrow{980\ ^{o}C} \underset{\text{amorphous spinel}}{SiO_2 + 2SiAl_2O_4}$$

$$\underset{\text{Amorphous spinel}}{SiO_2 + SiAl_2O_4} \xrightarrow{>1100\ ^{o}C} \underset{\text{mullite}}{1/3(3Al_2O_3.2SiO_2)} + \underset{\text{cristoballite}}{4/3(SiO_2)}$$

Step 1 is a very important step, and the temperature must be carefully controlled as the clay decomposed. The water given off by this reaction is not water remaining between the particles, but water bound into the mineral lattice. The loss of this water causes the lattice and hence the clay particles and therefore the clay briquette to shrink. If this step is not carefully controlled, the briquette can be destroyed by thermal stresses and by the rapidly escaping steam. The weight loss during step 1 is about 14% in pure kaolinite.

Steps 2 and 3 illustrate that the mineral undergoes further solid state reactions where the parent crystal is rearranged and silica is rejected in the form of a glass. Finally, at about 1100^{o}C, mullite and silica glass remains (**Chen *et al*., 2000**). The recrystallization points of the studied shale samples were showed by DTA thermograms.

5. Scanning electron microscope (SEM)

According to the SEM photomicrographs of the studied fired samples, the samples were classified into three grades:-

The first grade shows very fine cemented fragments of different phases (Fig.4), this is expected due to the high quality of these samples whether in water absorption, resistant to crushing strength and increasing in bulk density. This grade present in Heiz, Aswan, Gabal Hamza and Monkar El-Wahsh shales.

The second grade shows coarse cemented fragments (Fig.4), this is expected due to the medium quality of these samples whether in water absorption and resistant to crushing strength. This grade present in Bahariya and Mendishia shales.

The third grade shows holes due to bubbles formation (Fig.4), it could be evidence to bloating phenomena this may causes the decrease of the resistance to crushing strength and bulk density and increasing in water absorption and apparent porosity. This grade present in Wadi Natrun, Arish, Qasr El-Sagha and Sebaya shales.

Technological Characteristics (Table 3)

1. Water Absorption

The water absorption of the studied shale were done where the best result of minimum absorption were observed for Heiz (0.56%), Gabal Hamza (1.28%), Wadi Natrun (1.62%), Monkar El-Wahsh (2.93%) and Mendishia (5.88%) which make these samples matched with the standard value of water absorption according to **ES-56 :2005**, **EN-295 :2012** and **ZP-WN 295 :2013** where the maximum percent is 6%. The other shale samples not matched with standard values and these values were observed for Aswan (7.35%), Bahariya (10.38%), Sebaya (22.44%), Qasr El-Sagha (14.06%) and Arish (42.92%).

2. Bulk Density

The best results of maximum bulk density values were observed for Gabal Hamza (2.49 gm/cm^3), Heiz (2.42 gm/cm^3), Monkar El-Wahsh (2.39 gm/cm^3), Aswan (2.27 gm/cm^3), Mendishia (2.19 gm/cm^3), Bahariya (2.06 gm/cm^3) and Wadi Natrun shale (2.00 gm/cm^3). The shale samples of Sebaya (1.33 gm/cm^3), Qasr El-Sagha (0.93 gm/cm^3) and Arish (0.86 gm/cm^3) were not matched with the standard values of **SVCP** Company where the minimum value is 2.00 gm/cm^3.

3. Apparent Porosity

The best results of minimum apparent porosity were observed for El-Heiz (1.37%), Gabal Hamza (3.19%), Wadi Natrun (5.00%), Monkar El-Wahsh (7.02%), Mendishia (12.87%) and Aswan (16.67%). The samples of Sebaya (29.87%), Qasr El-Sagha (30.00%), Bahariya (21.43%) and Arish (36.72%) were not matched with the standard values of **SVCP** Company where the maximum value is 20.00%.

4. Modulus of Rupture (Dried Shale Samples)

All values of modulus of rupture (MOR) of the studied shale samples were matched with the standard limit of **SVCP** Company where the minimum value is 1 n/mm^2. The result for MOR values are Wadi Natrun (2.45 n/mm^2), Gabal Hamza (2.33 n/mm^2), Sebaya (1.87 n/mm^2) and Bahariya (1.58 n/mm^2), and medium values observed for Arish (1.47 n/mm^2), Qasr El-Sagha (1.38 n/mm^2), Mendishia (1.35 n/mm^2), Heiz (1.28 n/mm^2), Monkar El-Wahsh (1.22 n/mm^2), and Aswan (1.15 n/mm^2).

5. Modulus of Rupture (Fired Shale Samples)

The best result of maximum MOR were observed for Gabal Hamza (35.68 n/mm^2), Heiz (34.59 n/mm^2), Monkar El-Wahsh (32.96 n/mm^2), Wadi Natrun (31.29 n/mm^2) and Aswan (29.00 n/mm^2) shales. The shale samples of Sebaya (8.41 n/mm^2), Qasr El-Sagha (5.86 n/mm^2), Bahariya (9.78 n/mm^2), Mendishia (13.62 n/mm^2) and Arish (4.36 n/mm^2) were not matched with the standard values according to **EN-295 (2008)** where the minimum value is 25 n/mm^2.

6. Chemical Resistance

The shale samples of Aswan (0.12% loss on weight by acid and 0.1% loss on weight by basic), Mendishia (0.19% and 0.12%), Gabal Hamza (0.05% and 0.03%), Heiz (0.04% and 0.06%), and Monkar El-Wahsh (0.04% and 0.07%) have good resistance and were matched with vitrified clay pipes industry according to **EN-295:2013** (The maximum percent of loss on weight is 0.25%).

The shale samples of Bahariya (0.27% loss on weight by acid and 0.11% loss on weight by basic), Wadi Natrun (0.31% and 0.15%), Sebaya (0.42% and 0.31%), Qasr El-Sagha (0.38% and 0.13%), and Arish (0.40% and 0.32%) have low chemical resistance and not matched with the standard value (**SVCP** & **E.C., 2007**).

7. Volumetric Shrinkage

The best results of total shrinkage were observed for Aswan (6.11%), Gabal Hamza (10.7%), Wadi Natrun (7.71%), Monkar El-Wahsh (7.56%) and Heiz (9.31%) shale samples. These values were matched with the standard value of **SVCP** Company (5% minimum) and the other samples not matched with the standard value.

Conclusion

The study highlighted the feasibility of some Egyptian shale in the manufacture industries with producing vitrified clay pipes techniques. The parent shale can be vetrificated into crystalline phase after heat treatment, and the denser grain structure can be obtained by a suitable two-stage nucleation–crystallization process, nucleation at 400-500°C, followed by crystallization temperatures up to 940°C. With the increase of temperature from 526 to 588°C, the kaolinite was decomposed, and the amounts of two major crystalline phases have changed. The metakaolinite transformed into mullite at the higher crystallization temperatures (1100°C) in the studied shales based vitrified clay pipes.

The mineralogical analysis of the samples Heiz and Monkar El-Wahsh, taken in the outcrop of the Heiz and Daba'a formations, indicates the presence of the kaolinite as the main mineral, quartz and some other minerals in traces.

The technological characteristics of the studied shales decide that three shale samples were matched with vitrified clay pipes industry specifications (Heiz, Gabal Hamza and Monkar El-Wahsh shales). Four shale samples can use partially in blend mixed with high quality shales (Aswan, Mendishia, Bahariya and Wadi Natrun). The other three shale samples not confirmed in sewer pipes production (Qasr El-Sagha, Arish and Sebaya) because of some characteristics especially shrinkage percent, the bloating phenomena can destroy the geometrical design of product.

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Aperture (micron)	Monkar El-Wahsh	Heiz	Bahariya	Qasr El-Sagha	Sebaya	Gabal Hamza	Mendishia	Wadi Natrun	Aswan	Arish
<0.5	13.25	29.64	25.1	2.58	12.08	26.9	6.8	11.62	19.8	5.22
1 :0.5	10.87	23.4	12.98	15.26	18.1	19.22	24.32	16.35	9.06	3.54
01:02	9.67	20	13.5	12.68	5.11	5.3	5.21	6.21	2.35	1.43
02:03	4.19	0.3	2.7	7.5	8.1	4.21	6.25	1.2	4.45	8.54
03:04	7.84	6.1	5.1	8.14	1.5	6.25	6.7	0.68	2.35	1.35
04:05	10.25	0	2	14.36	3.15	8.24	1.03	2.5	9.54	3.2
05:06	11.02	3.59	1	5.36	2.15	9.89	2.14	1.98	8.32	1.2
06:07	5.36	1.76	3	8.27	8.36	5.1	8.5	2.3	7.16	1.48
07:08	10.72	1.46	1	2.9	4.29	8.9	7.3	7.8	9.24	5.4
08:09	2.14	0	0.58	1.26	7.46	0.15	5.11	4.32	8.47	8.35
09:10	1.36	1.42	15	0.78	3.65	0.25	6.5	11.26	1.65	4.5
10:15	4.21	0	5	0.15	6.11	1.2	1.23	10.25	5.54	12.25
15:45	3.14	0	7	0.39	3.68	2.3	3.21	7.5	6.5	25.25
63 :45	5.96	11.65	6.02	10.98	13.58	2.01	9.1	15.93	3.42	18.2
>63	0	0	0	9.35	2.58	0	6.5	0	2.1	0
Total	99.98	99.32	99.98	99.96	99.9	99.92	99.9	99.9	99.95	99.91

Table 1. Screen analysis of the studied shales.

locality	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	LOI	TDS	Total
Monkar El-Wahsh	59.8	17.9	0.2	5.5	2.5	2	0.95	0.26	0.9	9.8	2.6	99.81
Heiz	45.9	17.5	0.3	13.5	5	4	2	1.24	0.6	9.9	3.4	99.94
Bahariya	59.3	18.3	0.1	6.3	2.5	2	0.47	1.09	0.5	8.9	3.1	99.46
Qasr El-Sagha	55.6	16	0.3	9.5	3.3	2	1.36	0.9	0.2	10.5	3.9	99.66
Sebaya	56.7	14.2	0.4	12.7	3	2	1.72	1.04	0.4	7.8	4.6	99.96
Gabal Hamza	55.6	15.9	0.1	12.7	2.5	1.9	1.12	1.14	0.4	8.5	3.8	99.86
Mendishia	60.2	16.7	0.2	6	2.8	2	0.29	1.09	0.4	10.3	2.8	99.98
Wadi Natrun	57.3	11.5	0.1	12.7	2.5	2	0.9	1.62	0.3	11	4.1	99.92
Aswan	54.8	18.3	0.1	11.9	2.3	2.1	0.4	0.94	0.1	8.9	3	99.84
Arish	45.6	17.6	0.2	12.7	5	4.8	2.46	0.71	0.2	10.6	5.1	99.87

Table 2. Geochemical data of the studied shale samples (Major oxides wt. %).

Sample locality	Shrinkage %			L.O.I%	Apparent porosity %	W.A%	Bulk density (gm/cm^3)	Dry M.O.R (n/mm^2)	Fired M.O.R (n/mm^2)	Chemical resistance	
	Dry	Fired	total							H_2SO_4	NaOH
St. limits	1 min.	5 min.	5 min	NPD	20 max.	6 max.	2 min	1 min.	25 min.	Loss 0.0:0.25%	
Aswan	0.38	5.73	6.11	9.46	16.67	7.35	2.27	1.15	29	0.12	0.1
Mendishia	0.99	2.29	3.28	3.71	12.87	5.88	2.19	1.35	13.62	0.19	0.12
Bahariya	0.31	1.30	1.60	6.57	21.43	10.38	2.06	1.58	9.78	0.27	0.11
Gabal Hamza	1.60	9.08	10.7	7.94	3.19	1.28	2.49	2.33	35.68	0.05	0.03
Wadi Natrun	1.68	6.03	7.71	8.44	5.00	1.62	2.00	2.45	31.29	0.31	0.15
Sebaya	1.07	-0.46	0.61	10.45	29.87	22.44	1.33	1.87	8.41	0.42	0.31
Monkar El-Wahsh	0.15	7.40	7.56	8.29	7.02	2.93	2.39	1.22	32.96	0.04	0.07
Heiz	0.15	9.16	9.31	9.28	1.37	0.56	2.42	1.28	34.59	0.04	0.06
Qasr El-Sagha	1.76	DE	DE	9.41	30.00	14.06	0.93	1.38	5.86	0.38	0.13
Arish	1.68	DE	DE	10.88	36.72	42.92	0.86	1.47	4.36	0.4	0.32

Table 3. Summary of the technological characteristics of the studied shales.

ISSN 2348 – 7968

Fig.1. Location map of the studied composite shale samples.

ISSN 2348 – 7968

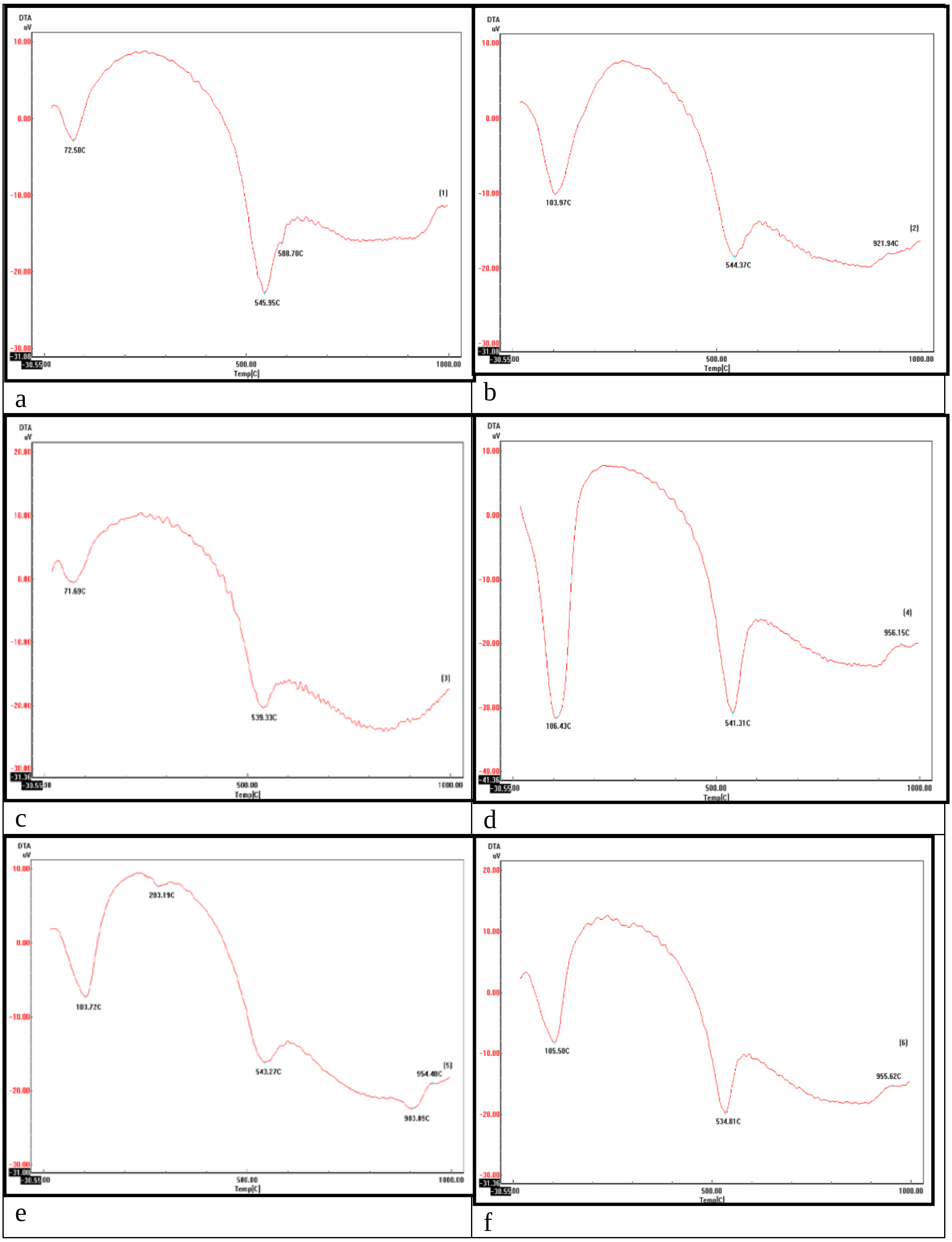

Fig. 2(a-f). DTA pattern of the studied shales.

a- Bahariya	b- Qasr El-Sagha
c- Heiz	d- Wadi Natrun
e- Sebaya	f- Gabal Hamza

ISSN 2348 – 7968

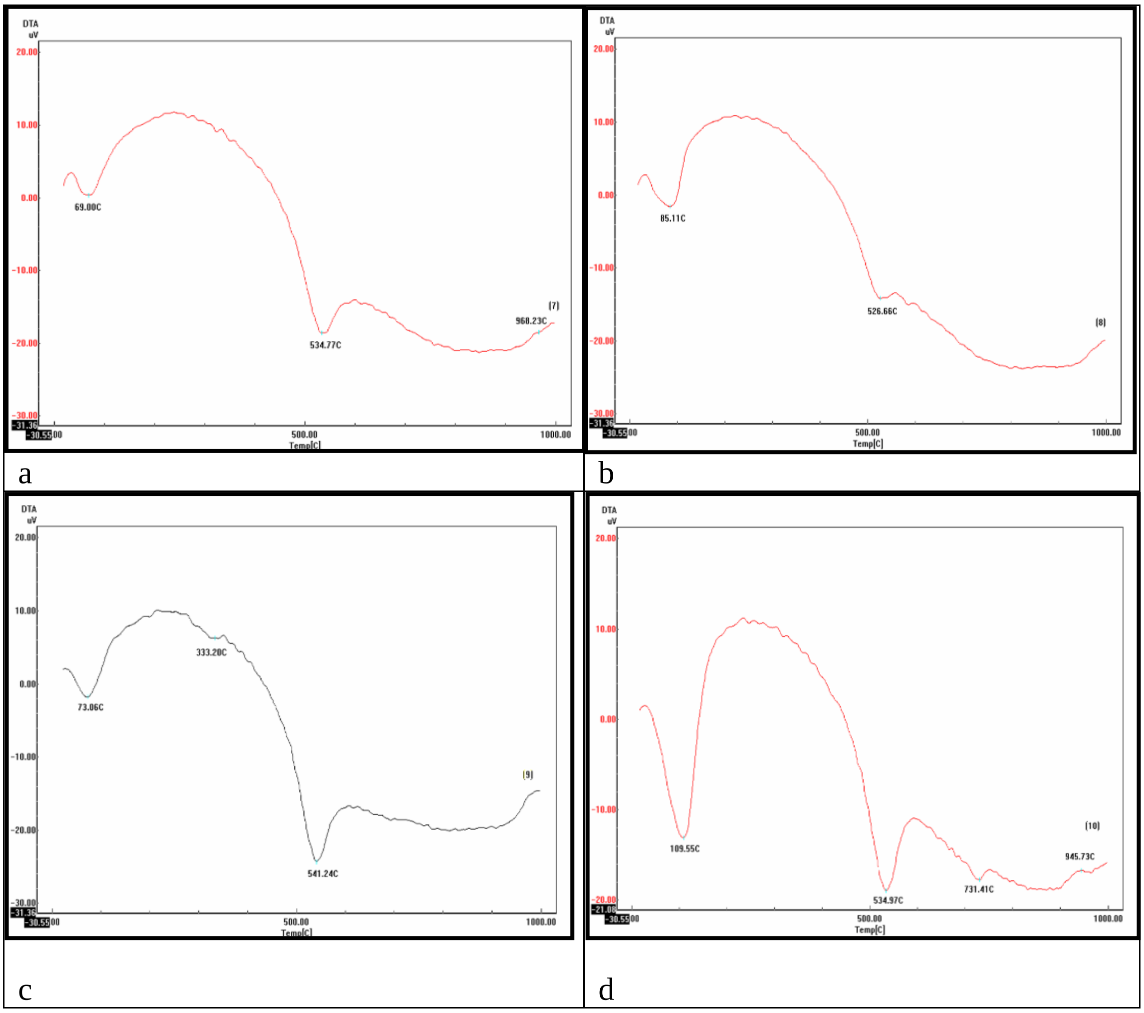

Fig. 3(a-d). DTA pattern of the studied shales.

a- Monkar El-Wahsh b- Mendishia

c- Aswan d- Arish

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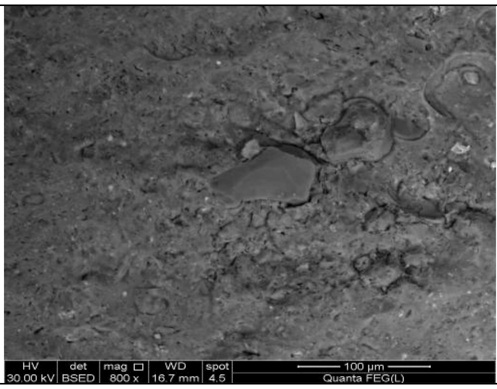
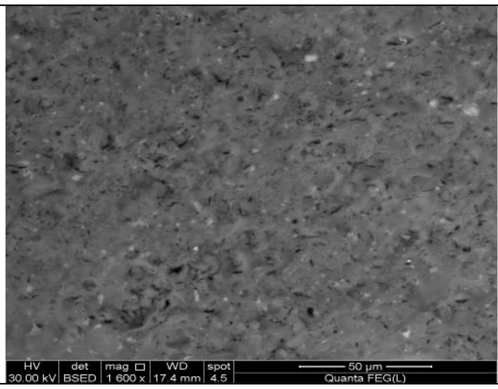
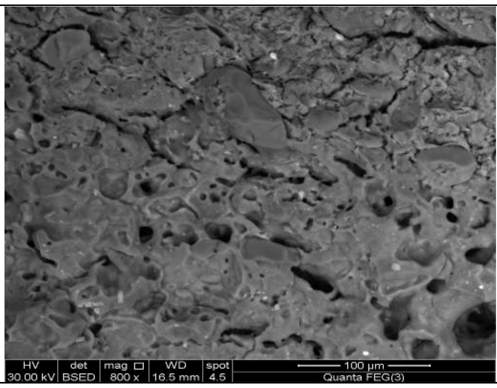
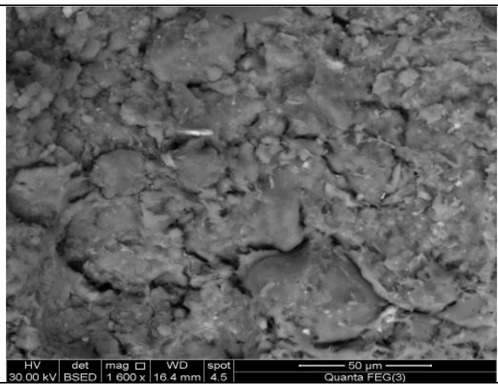


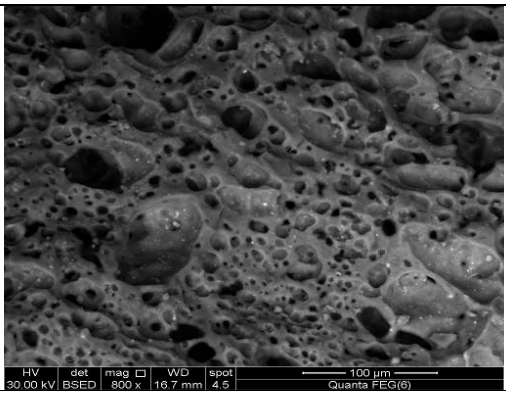


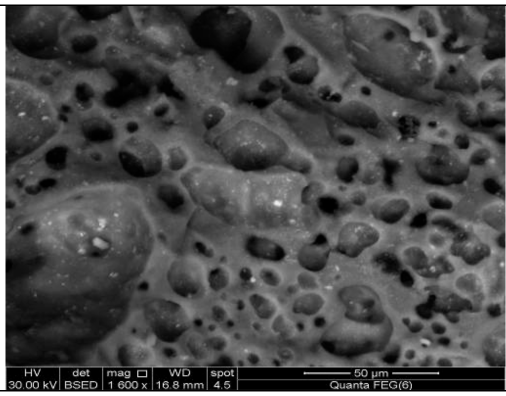
Heiz shales





Bahariya shales





Sebaya shales

Fig.4. Close up view of SEM photomicrograph showing some shale samples fired at 1200°C.