Journal of Thermal Analysis, Vol. 46 (1996) 1421-1435

COMBINED THERMAL AND STRUCTURAL STUDY OF SOME EGYPTIAN BENTONITIC CLAYS

A. M. El-Shabiny, S. M. Hammad, I. A. Ibrahim and A. K. Ismail**

Physics Department, National Research Centre, Dokki, Cairo, Egypt
*CMRDI, El-Tebbin, Helwan, Cairo, Egypt

Abstract

Egyptian bentonitic clays from Qasr El-Sagha, Wadi El-Rayan, Kom Oshim and the Cairo – Alexandria desert road were studied thermally (TG, DTG and DTA) and structurally (XRD and IR). The clay fraction consisted mainly of montmorillonite, kaolinite and some illite. Gypsum, quartz and calcite were also identified. It was found that the Na- to Ca-montmorillonite ratio increases in the following sequence: Qasr El-Sagha<Wadi El-Rayan<Kom Oshim<Cairo – Alexandria desert road. There is a marked concentration of gypsum, the highest amount occurring in the bentonite from Qasr El-Sagha, and the least in that from the Cairo – Alexandria desert road. Calcite was mainly found in Kom Oshim, with a very small amount from the Cairo – Alexandria desert road. Magnesium is more abundant than iron in the octahedral layer and increases in the following sequence: Cairo – Alexandria desert road<Kom Oshim<Wadi El-Rayan<Qasr El-Sagha.

Keywords: bentonitic clay, IR spectroscopy, thermal analyses, X-ray diffraction

Introduction

Bentonites are mainly composed of montmorillonite (smectite), together with some other clay and inorganic minerals. Smectite is really the name for a group of minerals, all of which display the startling property of being able to expand and contract their structure while maintaining crystallographic integrity. Structurally, montmorillonite mineral is composed of repeated units of $Al_4Si_8O_{20}(OH)_4$, which are loosely held together with water between them. Substitution usually occurs in either the octahedral or the tetrahedral sheet, and extensive replacement gives rise to a number of modifications with a variety of compositions [1]. Owing to this isomorphous replacement of ions within the structure, the montmorillonite lattice becomes negatively charged, with the layer charge ranging from approximately 0.2 to 0.6. The negative character is balanced by cations, which are held on the surface of the flakes, and consequently they are readily exchanged. The cations most commonly found in nature are sodium and calcium.

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

The properties of the primary mineral in bentonite, that is smectite, are still a subject of research in pursuit of ways to improve its behaviour in industrial applications [2]. The greatest use of bentonite in industry results from its swelling action in water. Two of its primary used are for making a drilling mud and as a bonding agent for moulding sands uses in foundries. Acid-activated bentonite is marketed for use as a decolouring agent for oils and as a catalyst for petroleum. Bentonite clay is used in Egypt in great quantities; it is present in huge reserves in the El-Fayoum area, Sinai, El-Alamein, New Valley and along the Cairo – Alexandria desert road. However, the quality and quantity of the ores are still questionable.

One method of analysis is usually not sufficient to characterize such earthy material and a combination of different methods is required. Therefore, this work aims at the characterization of some Egyptian bentonitic clays, by using both thermal and structural studies. The ores were characterized by applying thermal analyses (DTA, TG and DTG), X-ray diffraction (XRD) and infrared (IR) spectroscopy. Through a joint evaluation of the results from the different techniques, semi-quantitative pictures of the samples and of the octahedral substitution can be obtained. The results will be of help in the selection of the suitable locality and proper treatment for specific applications.

Experimental

Materials

Four bentonitic samples were studied, three of them from different localities in the El-Fayoum area (Qasr El-Sagha, Wadi El-Rayan and Kom Oshiem) and the fourth from the Cairo – Alexandria desert road. These materials were denoted 1, 2, 3 and 4, respectively. The chemical compositions of the samples were determined by the standard chemical analysis techniques for clay and are given in Table 1.

Table 1 Chemical analysis (wt.%) of the bentonitic samples

Sample	SO_3	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Cl
1	2.04	52.88	17.11	7.80	4.18	2.03	1.25	0.01
2	0.27	47.01	22.51	8.24	1.42	1.00	0.98	2.91
3	0.73	49.87	21.04	9.07	2.58	1.58	1.09	0.22
4	0.08	55.09	21.81	7.05	0.42	1.89	0.55	1.24

Procedure

TG, DTG and DTA were carried out on the as-received (untreated) samples in the ambient atmosphere (air) from room temperature up to 1200°C at a heating rate of 10°C min^{-1}.

X-ray diffraction analysis was performed with a Dyano diffractometer (Model XRD 8000), using monochromatic CuK_α radiation at 35 kV and 15 mA and a scanning speed of 2°(2θ)/min. There is no single way to prepare clay minerals for XRD analysis. However, there must be a single procedure of preparation for a given set of samples. The procedure used in this work was taken from Koeble [3], Brown and Brindley [4] and Moore and Reynolds [5]. Accordingly, four specimens were prepared for each bentonitic sample:

a) Untreated specimen (as-received): No treatment was carried out.

b) Oriented specimen: Oriented aggregates of clay were allowed to settle down onto a flat glass slide from the suspension of the clay components of fine grains.

c) Glycerol-treated specimen: The oriented specimen was moistened with glycerol by subjecting it to glycerol vapour for about an hour.

d) Heat-treated specimen: The oriented specimen was heated for 3 h at 650°C, then cooled in the furnace to room temperature. The results of thermal analyses were used to specify the temperature of the heat treatment.

The IR spectra (transmittance) were recorded on a Beckman spectrophotometer (Model 42509), using the KBr disc technique in the wavenumber range from 200 to 4000 cm^{-1}.

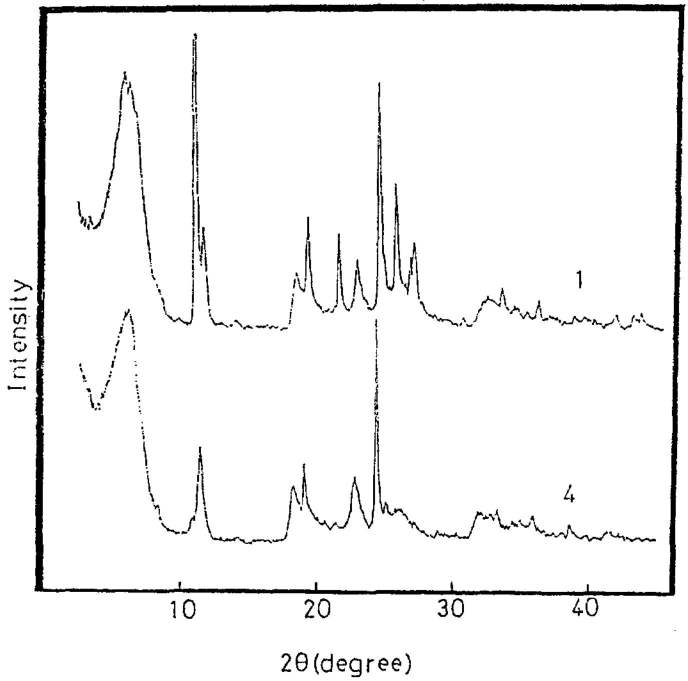

Fig. 1 X-ray diffractograms of samples from El-Fayoum area, Qasr El-Sagha (sample 1) and Cairo - Alexandria desert road (sample 4)

Results and discussion

Structural characteristics

X-ray diffraction analysis

The X-ray diffractograms of the untreated specimens for the samples from the El-Fayoum area (1) and the Cairo – Alexandria desert road (4) are shown in Fig. 1. The calculated interplanar spacings and the relative intensities of the four samples are given in Table 2. The broadening of the peak characterizing the clay mineral indicates that the clay fraction possesses a small grain size, i.e. poor crystallinity. Clay minerals are better identified by basal (001) reflections. The (*hkl*) peaks are not very diagnostic because the structures of most of them are very similar in their *x*- and *y*-directions. It is the atomic pattern along the

Table 2 XRD data of the as received specimens of samples from Qasr El-Sagha (2), Kom Oshim (3) and Cairo – Alexandria desert road (4)

1		2		3		4	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
14.25	66	13.85	100	13.85	95	13.23	75
9.85	10	9.76	15	9.74	10	9.67	12
7.46	100	7.49	30	7.45	42	7.48	8
7.13	32	7.07	92	7.04	100	7.07	42
4.42	16	4.41	60	4.39	40	4.46	24
4.24	35	4.24	40	4.22	49	4.25	34
3.80	29	3.80	5	3.79	14	–	–
3.57	21	3.57	67	3.49	54	3.57	28
3.36	78	3.35	86	3.35	95	3.36	100
3.30	20	3.29	15	3.29	20	3.25	19
3.20	47	3.20	6	3.21	31	–	–
3.09	22	–	–	3.17	11	3.13	14
3.03	26	3.04	22	3.04	33	–	–
2.692	5	2.832	34	–	–	–	–
2.554	9	2.580	25	2.575	21	2.564	11
–	–	–	–	2.508	20	–	–
2.481	12	2.476	20	2.466	18	2.478	12
–	–	2.362	21	–	–	–	–
2.302	8	–	–	–	–	2.302	10
2.066	3	1.986	17	–	–	2.150	6
1.947	3	–	–	–	–	–	–
1.903	9	–	–	–	–	–	–

z-direction that is the most different from one structure to another. In the present work, we have used information from the JCPDS powder diffraction files and the calculated diffraction patterns by computer program modelling [5–7]. From the diffraction data, mainly montmorillonite, kaolinite and illite were identified. Montmorillonite was identified by the d-spacing in the range 13–15 Å and 3.5–3.6 Å, and illite by d-spacings of 9.9–10 Å and 4.5–5 Å. Besides the clay minerals, quartz, gypsum and calcite were also present. Quartz was identified by its 3.34 and 4.26 Å spacings. Gypsum and calcite were mainly identified by their strongest line, at 7.56 and 3.04 Å, respectively, as well as by their weaker diffraction lines. The strongest gypsum line is shown in sample 1. This was reflected in the chemical analysis (Table 1) as high amounts of SO_3 and CaO.

The XRD patterns after the different treatments are shown in Fig. 2 for sample 1 as a representative one. It is worthy of mention that only the clay fraction was observed. The XRD data on the four samples are given in Table 3. For the glycerol-treated specimens, the presence of montmorillonite was confirmed by expansion of the 13–15 Å. The kaolin group was identified by the d-spacings 7.1–7.2 Å spacing to 17–18 Å. On the other hand, the presence of kaolinite and illite was confirmed by the absence of lattice expansion in their characteristic

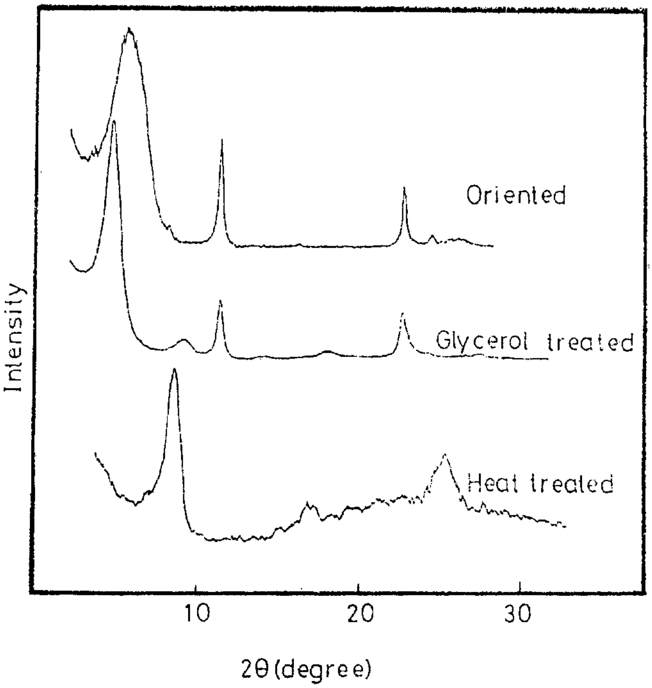

Fig. 2 X-ray diffractograms of sample from Qasr El-Sagha (sample 1) with different treatments

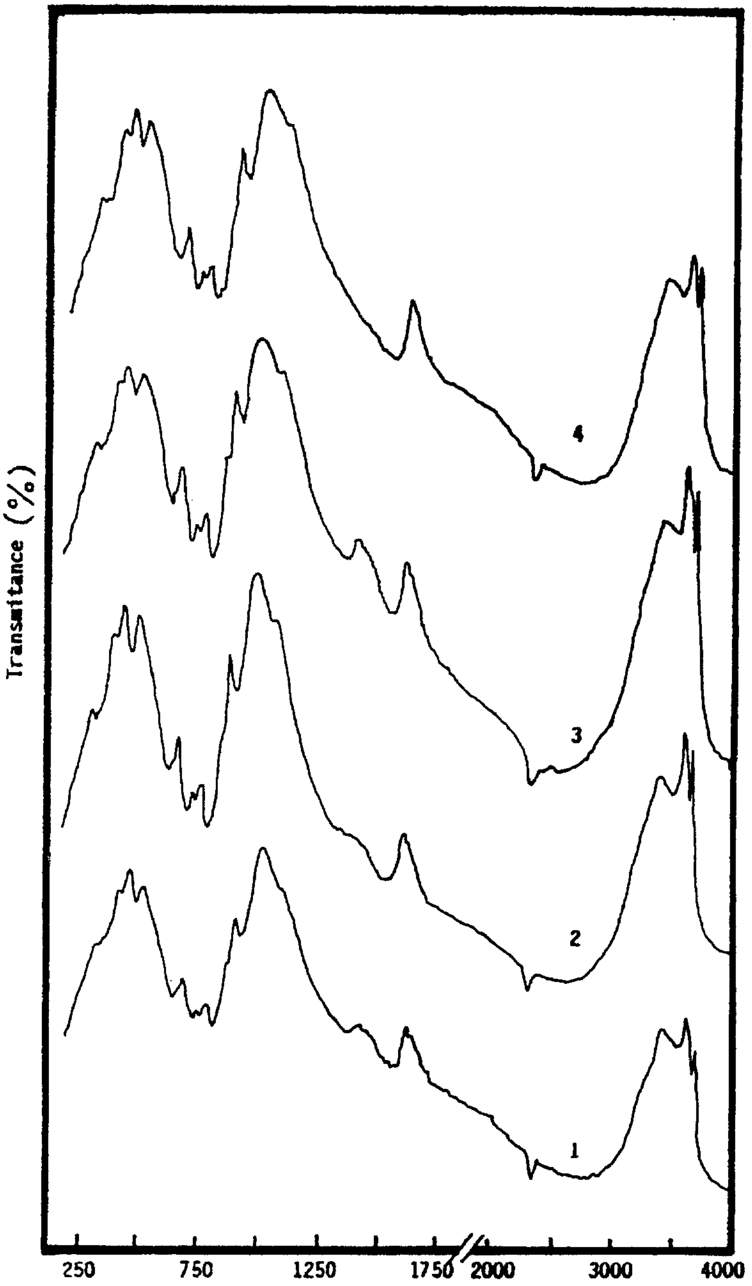

Fig. 3 IR-bands of bentonitic samples: (1) Qasr El-Sagha, (2) Wadi El-Rayan, (3) Kom Oshien and (4) Cairo – Alexandria desert road

Table 3 XRD data of the oriented, glycerol treated and heat treated specimens of the four bentonitic samples

Oriented							
Sample 1		Sample 2		Sample 3		Sample 4	
d/Å	I/I_o	d/Å	I/I_o	d/Å	I/I_o	d/Å	I/I_o
–	–	–	–	–	–	–	–
15.02	100	15.15	100	17.59	76	14.77	100
9.87	5	9.87	19	9.87	6	9.87	10
–	–	–	–	–	–	–	–
7.15	31	7.15	98	7.15	100	7.18	61
–	–	4.97	2	–	–	4.97	2
–	–	–	–	–	–	–	–
3.59	15	3.60	40	3.60	47	3.60	37
3.34	2	3.35	10	3.35	2	3.34	6
–	–	–	–	–	–	–	–
Glycerol treated							
17.67	100	18.03	100	18.03	100	17.67	100
–	–	–	–	–	–	–	–
9.86	7	9.76	6	9.87	6	–	–
8.97	10	9.07	11	9.01	11	8.89	7
7.18	20	7.18	78	7.18	78	7.15	17
5.86	2	5.86	4	5.87	4	5.86	2
4.48	16	4.54	8	4.48	8	4.50	5
3.62	18	3.60	62	3.60	62	3.60	23
3.37	7	3.38	8	2.28	8	3.37	2
2.99	2	3.00	3	1.99	3	3.00	2
Heat treated							
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
9.87	100	9.64	100	9.55	100	9.54	100
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
4.89	13	4.84	10	4.84	25	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
3.37	23	3.34	24	3.70	10	3.42	37
3.28	3.	3.23	33	3.18	31	3.23	48

peaks. More confirmation was obtained from the heat-treated specimens. The diffraction lines of montmorillonite (≈14.9 Å) and kaolinite (≈7.15 and 3.60 Å) in the oriented specimens disappeared on heating at 650°C. The *d*-spacing of illite at about 10 Å did not show any considerable change upon heating.

The ratio of the Ca- to the Na-form of montmorillonite can be estimated from the value of the basal reflection. The Ca-form shows a basal reflection at 15.0 Å (JCPDS card No. 13–135), while the Na-form gives the same reflection at 13.6 Å (JCPDS card No. 29–1498). The presence of a pure form of bentonite is not expected; a mixed type is more usual. From the values of the basal interplanar spacings, the samples were classified according to the sequence of increase of the Na- to the Ca-form ratio as follows: Qasr El-Sagha (1)-<Wadi El-Rayan (2)<Kom Oshim (3)<Cairo – Alexandria desert road (4).

Infrared spectroscopic analysis

The IR spectra of the four bentonitic samples are shown in Fig. 3, and the frequencies (wavenumbers, cm^{-1}) of the absorption bands are given in Table 4. All four samples absorb IR at the same frequencies, but with different intensities. One advantage of IR spectroscopy is that amorphous silica can be identified [8], and not only the crystalline forms as in phase analysis by XRD. It has

Table 4 Wavenumbers (cm^{-1}) of the IR absorption bands

Sample 1	Sample 2	Sample 3	Sample 4
3690	3685	3700	3700
3610	3610	3695	3620
3425	3425	3440	3450
1627	1627	1637	1637
1434	1420	1436	–
1100	1100	1104	1109
1010	1011	1030	1017
905	909	920	914
872	874	880	–
790	790	799	799
745	749	756	753
686	686	693	693
519	527	525	530
459	459	465	466
414	420	438	422
326	328	340	330

also been shown [9] that the range of IR used can give information about the substitution in the octahedral layer of the clay minerals in the samples.

The broad absorption band with maximum at about 3440 cm^{-1} and the band near 1640 cm^{-1} are due to the OH-valency vibration of water absorbed on the surface of the clay minerals. These two bands of molecular water were present within the ranges 3450–3425cm^{-1} and 1635–1625 cm^{-1} in all records. Two other overlapping bands between 4000 and 3600 cm^{-1} resulted from the valency vibration of OH^- ions in the clay mineral. The band near 3680 cm^{-1} is specific for kaolinite. The band near 910 cm^{-1}, which is due to the $H-O...Al^{3+}$ group of clay minerals [10], was present within the range 905–920 cm^{-1} in all the records. However, the band near 938 cm^{-1}, which is due to $H-O...Fe^{3+}$, was absent from all the records. This means that iron is present mainly as oxides. The band near 870 cm^{-1} represents OH groups bound to one iron and one aluminium or magnesium neighbour [10]. This band was present in the range 880–872 cm^{-1}, but absent from sample 4, which has the lowest Fe_2O_3 content, as proved by the chemical analysis (Table 1). It was also shown that the bands near 540 cm^{-1} were recorded between 530 and 519 cm^{-1} and those near 750 cm^{-1} were recorded between 756 and 745 cm^{-1}. According to Hayashi and Oinuma [9], the wavenumbers of the bands near the regions 540–560 and 744–765 cm^{-1} decrease with the increase of Mg and/or Fe in the octahedral position. From Table 4, such substitution therefore increased in the sequence: Cairo – Alexandria desert road (4)<Kom Oshiem (3)<Wadi El-Rayan (2)< Qaser El-Sagha (1). However, Mg is more abundant than Fe in the octahedral layer, as indicated by the absence of the 938 cm^{-1} band.

The bands near 1440 and 870 cm^{-1} reflect the characteristic absorption of carbonate (CO_3); they are found in all samples except sample 4. This is in accordance with the results of X-ray analysis: calcite was not identified in this sample. From the results of X-ray and IR analyses, calcite was present in the following sequence: Cairo – Alexandria desert road (4)<Qaser El-Sagha (1)= Wadi El-Rayan (2)<Kom Oshiem (3).

Thermal analyses

The DTA curves of the four samples are shown in Fig. 4 and the endo- and exothermic peaks are identified in Table 5. The samples are generally characterized by the presence of two large and broad endothermic peaks in the temperature ranges 130–140°C and 550–560°C. The first peak (≈135°C) is due to the hygroscopic water usually exhibited by montmorillonite. The peak at about 555°C is better defined than the first one and represents the dehydroxylation of kaolinite and montmorillonite [11].

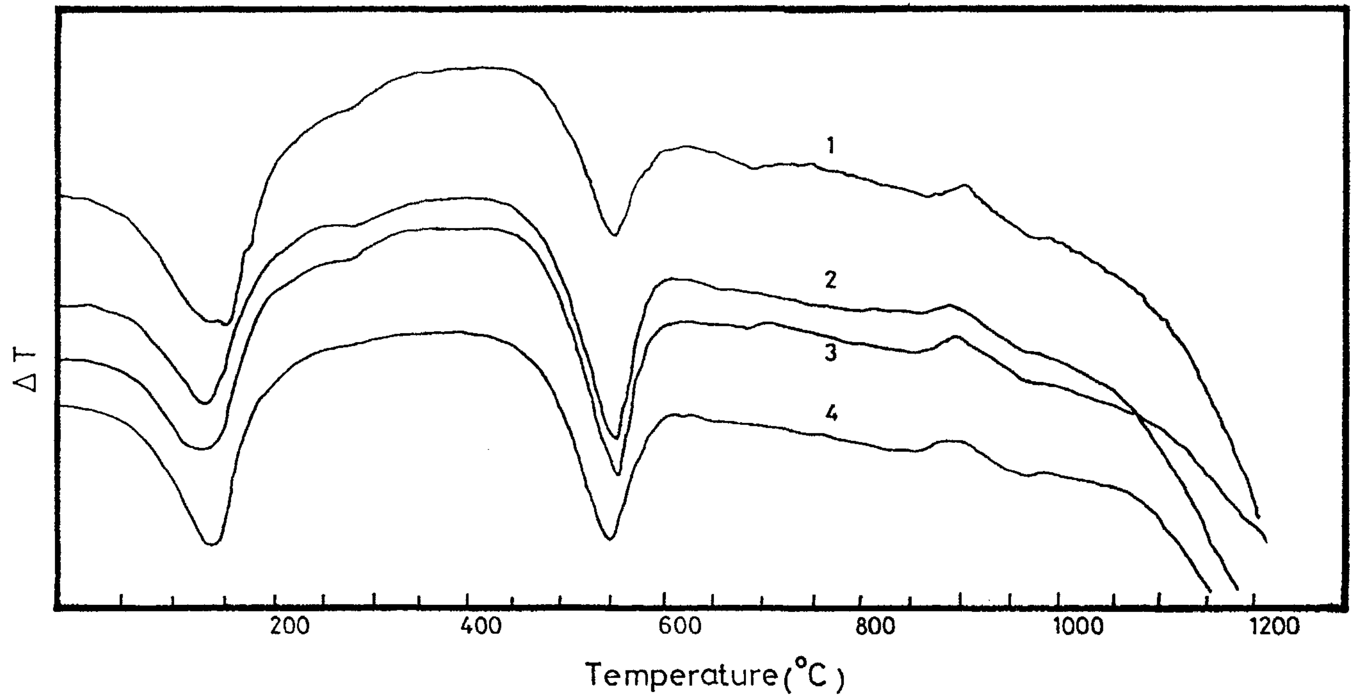

Fig. 4 DTA curves of bentonitic samples: (1) Qasr El-Sagha, (2) Wadi El-Rayan, (3) Kom Oshien and (4) Cairo – Alexandria desert road

Table 5 DTA and DTG data

Sample	DTA /°C							DTG /°C					
	Endo						Exo						
1	140	145	175	280	555	715	915	140	155	170	280	560	1200
2	135	–	–	280	560	–	900	135	–	–	280	560	–
3	130	–	–	280	560	700	905	130	–	–	280	560	1205
4	135	–	–	–	550	–	910	140	–	–	–	555	–

Other endothermic peaks were recorded at 145 and 175°C (sample 1) and at 280°C (samples 1, 2 and 3). The dehydration peaks in the temperature range 145–280°C relate to the removal of water of crystallization from gypsum. The sequence of dehydration is from $CaSO_4{\cdot}2H_2O$ to $CaSO_4{\cdot}1/2H_2O$ and finally to anhydrous $CaSO_4$. The weak endothermic peak at about 705°C is probably due to the abnormal illite observed by Mackenzie *et al.* [12]. Only one exothermic peak was observed for the four samples in the temperature range 900–915°C, characteristic for kaolinite.

Table 6 Percentage loss in mass (TG)

Sample	Temperature range /°C				Total loss
	<285	400–750	750–1000	>1000	
1	9.9	5.2	0.4	2.5	18.5
2	8.7	7.9	0.9	0.6	18.1
3	8.8	6.9	0.6	1.2	17.5
4	9.5	6.0	0.4	0.2	16.1

The TG and DTG curves are shown in Figs 5 and 6, respectively. The peak at about 1200°C in the DTG diagram (Table 5) is due to the decomposition of gypsum. However, this decomposition reaction did not appear in the DTA curves because of the sharp descent in the DTA curve, due to the shrinkage of the sample at high temperatures [13]. The losses in mass associated with the above-mentioned solid-state reactions are given in Table 6.

A reasonable semi-quantitative estimation of the minerals present is possible by integrating the thermal quantitative analysis (TG) and X-ray results. The mass losses give directly the proportion of gas (H_2O, CO_2 or SO_3) evolved from the material. In the present work, the dehydroxylation of clay minerals and the decomposition of calcite and gypsum were considered. When divalent iron and/or manganese are present, their oxidation may lead to an increase in mass and thereby to a reduction in the apparent mass loss. The intensities of the XRD lines may help in the identification of this interference.

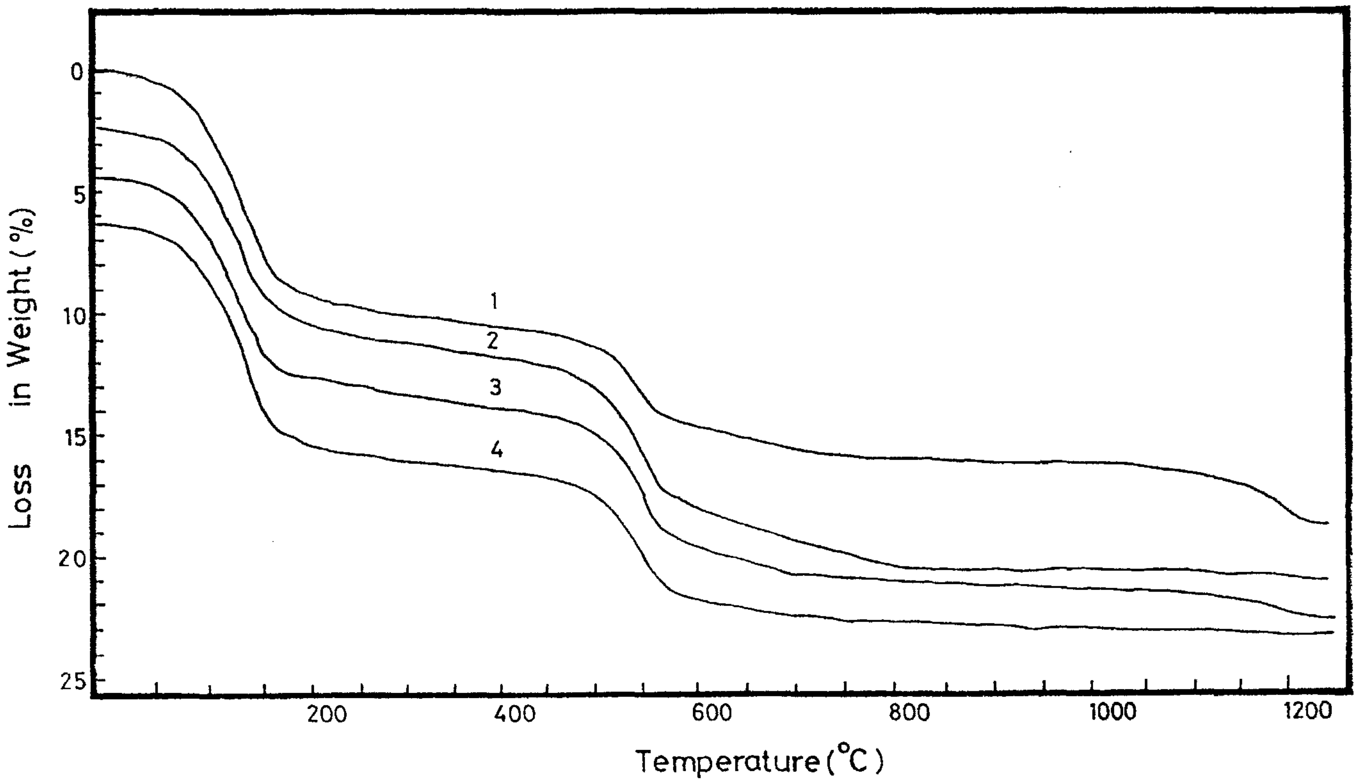

Fig. 5 TG curves of bentonitic samples: (1) Qasr El-Sagha, (2) Wadi El-Rayan, (3) Kom Oshien and (4) Cairo --Alexandria desert road

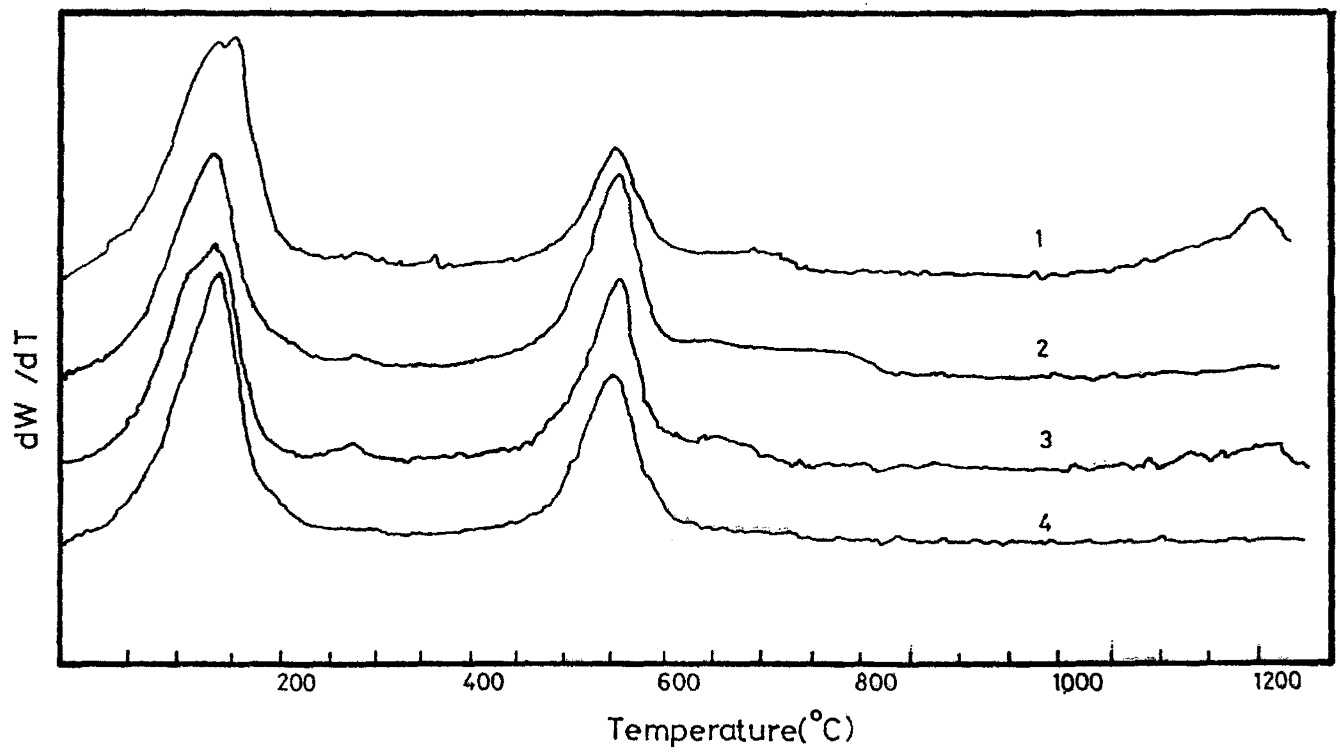

Fig. 6 DTG curves of bentonitic samples: (1) Qasr El-Sagha, (2) Wadi El-Rayan, (3) Kom Oshien and (4) Cairo - -Alexandria desert road

Table 7 Amounts of calcite and gypsum in wt.%

Sample	Gypsum	Calcite
1	5.4	0.9
2	1.3	2.0
3	2.6	1.4
4	0.4	0.9

Quantitative estimation of the clay fraction, calcite and gypsum, is possible if the loss in mass in the temperature range 400–750°C is considered to be due to the dehydroxylation of clay components [5], while that in the range 750–1000°C and above 1000°C is due to the decomposition of calcite and anhydrous $CaSO_4$, respectively. However, since it is not easy to calculate the molecular weight of each clay mineral because of the many possibilities of substitution inside the lattice [1], only estimation of relative values is possible. From the TG results in Table 6, the clay fraction increases in the following sequence: Qaser El-Sagha (1)<Cairo – Alexandria desert road (4)<Kom Oshiem (3)-<Wadi El-Rayan (2). This estimation, the chemical analysis and the X-ray results together indicate that Al_2O_3 is practically not present in free form; it exists as aluminosilicates in the clay fraction. From the ratios of the molecular weight of calcite ($CaCO_3$) to that of CO_2 gas, and of that of gypsum ($CaSO_4 \cdot 2H_2O$) to that of SO_3 gas, and also the loss in mass in the respective temperature range, the amounts of the two components were calculated. They are given in Table 7. The amount of gypsum increases in the following sequence: Cairo – Alexandria desert road (4)<Wadi El-Rayan (2)<Kom Oshiem (3)< Qaser ElSagha (1), in agreement with the results of chemical and X-ray analyses. On combination of the results of XRD and IR analyses with those of TG, calcite was concluded to increase in the following sequence: Cairo – Alexandria dessert road (4)=Qaser El-Sagha (1)< Kom Oshiem (3)<Wadi El-Rayan (2).

References

1 G. W. Brindley, 'Crystal Structure of Clay Minerals and their X-ray Identification', ed. G. W. Brindley and G. Brown, Mineralogical Soc., London, No. 5, 1980, p. 170.
2 D. Plee, L. Gatineau and J. J. Fripiat, Clays and Clay Minerals, 35 (1987) 81.
3 E. F. Koeble: 'Handbook of X-rays', Mcgraw-Hill Book Company, London 1967.
4 G. Brown and G. W. Brindley, Ref. [1], p. 305.
5 D. M. Moore and R. C. Reynolds, Jr., 'X-ray Diffraction and the Identification and Analysis of Clay Minerals', Oxford Univ. Press. Oxford, New York 1989.
6 R. C. Reynolds, Jr., Ref. [1], p. 249.
7 C. M. Bethke and R. C. Reynolds, Jr., Clays and Clay Minerals, 34 (1989) 224.
8 M. Fields, I. K. Walker and P. P. Williamy, J. Sci. Tech., (1956) 38.
9 H. Hayaski and K. Oinuma, Am. Mineral. 50 (1965) 476.
10 J. M. Sterratosa, Am. Mineral, 45 (1960) 1101.

11 R. W. Grimshow, E. Heaton and E. L. Roberts, Trans. Brit. Cer. Soc., 44 (1945) 69.
12 R. C. Mackenzie, G. F. Walker and R. Hart, Mineral. Mag., 28 (1949) 704.
13 R. C. Mackenzie, 'Some Advanced Topics in Clay Mineralogy and in Differential Thermal Analysis', Soil Sci. Dep., Fac. Agr., Cairo University, 1967.