Thermochimica Acta, 43 (1981) 1—7
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THE USE OF WADI GHARANDEL CLAY DEPOSITS FOR THE MANUFACTURE OF VARIOUS CERAMIC PRODUCTS. I. ASSESSMENT OF THE RAW MATERIALS

ATIA M. KABESH and ABDEL-AZIZ A. KHALIL

Refractories and Building Materials Laboratory, National Research Centre, Dokki, Cairo (Egypt)

(Received 10 June 1980)

ABSTRACT

The reconstruction of Sinai, A.R. Egypt, has now become one arised now of the main problems on the national scale. The authors tried to make use of the huge and extensive deposits of wadi gharandel clay formations for making building bricks, ceramic tiles, pipes, etc. The mineral and chemical constituents of three samples were determined using DTA, TG and X-ray diffractometry in addition to chemical analysis. Briquettes were made by hand moulding and extrusion and fired at 900°C. The evaluation of the raw materials was carried out by determining the physical properties of the fired bodies. Results indicate that the investigated clays are of the illitic type with varying amounts of montmorillonite and kaolinite as well as a small amount of quartz. In addition, samples I, II and III contain some feldspar, while only samples II and III contain calcite and gypsum contaminations. Firing properties suggest that sample I could be used for the production of stoneware, mainly tiles. Samples II and III, however, are suitable for making building bricks.

INTRODUCTION

Little work has been carried out on the Sinai clay deposits, except the kaolines which have been extensively studied and used for refractory [1] and porcelain [2] industries. On the basis of chemical analysis alone, early studies on the suitability of wadi gharandel clay formations for the production of sulphuric acid and portland cement by the Müller—Külne process have been made since 1958 [3].

As far as the authors are aware, little work has been done on the possible use of wadi gharandel clays for making ceramic products. This induced the authors to carry out the present study to assess the suitability of these raw materials for producing such items. Three different samples were taken and their mineral and chemical constituents were thoroughly investigated. Briquettes were prepared and fired at 900°C, the average temperature used for various low temperature ceramics (mainly bricks). The physical properties of the fired bodies were also determined to assess the possible utility of such raw material in producing ceramic products of good quality.

0040-6031/81/0000—000(/$02.50 © 1981 Elsevier Scientific Publishing Company

EXPERIMENTAL

Materials

Three samples of the clay deposits representing different locations in the wadi gharandel locality, Sinai peninsula, A. R. Egypt, were supplied (50 kg each) by the General Company for Petroleum. Quartered representative samples were taken and ground to —100 mesh B. S. sieve to be used for the constitution investigations only. Clay lumps were slaked with water 24 h prior to the preparation of the briquettes.

Procedure

Differential thermal analysis (DTA), thermogravimetry (TG) and X-ray diffractometry investigations were carried out following the published work on the clay mineralogical identifications [4—8]. Non-clay minerals were further investigated by scanning the coarse fraction (>63 μm) of water-leached samples. Exactly-weighed samples were used throughout the investigations for a semi-quantitative work and to facilitate comparison. Chemical analysis, on the other hand, was carried out in accordance with the conventional silicate analysis techniques. The alkalies (Na_2O and K_2O) were determined by flame photometry, and the Fe_2O_3, in the fusion cake of the R_2O_3, by direct titration with EDTA.

Briquettes were prepared by hand moulding (75 × 75 × 75 mm) and extrusion (25 × 50 × 60 mm), using each clay raw material as the sole constituent without any other additions. The prepared bodies were dried for 7 days under laboratory conditions, then for 24 h in an electric drying oven at 110°C and fired for 1.5 hours at 900°C. Care was taken during the first 300°C of heating by selecting a very slow rate of about 1°C min^{-1} to avoid the sudden evolution of the mechanically-held water of the clays which was found to greatly affect the compactness of the bodies, thus forming deformation and cracks.

The physical properties of the fired bodies were determined in accordance with the international specifications for testing ceramic bodies [9]. The properties determined were the bulk density, apparent porosity, water absorption, linear shrinkage and compressive strength.

RESULTS AND DISCUSSION

Composition

Differential thermograms of the investigated samples (Fig. 1) show three main thermal effects: two large endotherms at about 180 and 560°C and a high temperature exotherm at about 930°C. These thermal effects characterize the presence of illite mineral as the main constituent, in accordance with the published work of various investigators [5,6]. The rational amounts of the two endotherms, however, indicate that montmorillonite coexists in

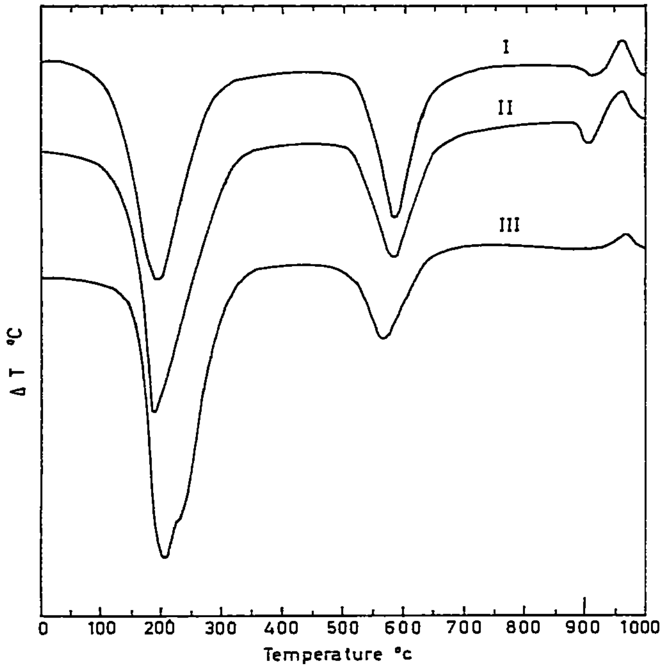

Fig. 1. Differential thermal analysis of wadi gharandel clays.

appreciable amounts in all the studied clays. Samples II and III exhibit small additional thermal effects. Sample II shows an endo effect at about 890° C, denoting the presence of calcite contaminations, while sample III reveals an endothermic shoulder at about 220° C, following the first large endotherm of the clay which is related to the presence of gypsum impurities [10]. It should be noticed, however, that the exotherm shown by sample III is smaller than that of samples I and II. The difference may suggest that the occurence of a small additional endotherm at nearly the same temperature range may be caused by the presence of some calcium carbonate impurities. It could be concluded that sample I contains neither gypsum nor calcite impurities while samples II and III contain various amounts of the two accessory minerals.

Results of the thermogravimetric analysis are shown in Fig. 2 from which it is clear that the investigated clays reveal two main weight loss steps: the first (20—200° C) corresponds to the liberation of the mechanically-held water, about 12% loss; the second stage lies between 500 and 700° C which characterizes the evolution of the lattice hydroxyl groups of the clays. However, it should be noticed, that samples II and III reveal a marked increase in weight loss in the two stages compared with sample I. The difference in the first stage (<300° C) could be related to the presence of gypsum impurities in both samples, being high in sample III. The high temperature weight loss of sample II is again larger than sample III and both are more than sample I. This variation could be attributed to the presence of calcium carbonate contaminations in samples II and III. The TGA results confirm the previous deductions of DTA. The presence of gypsum in sample II, however, was not

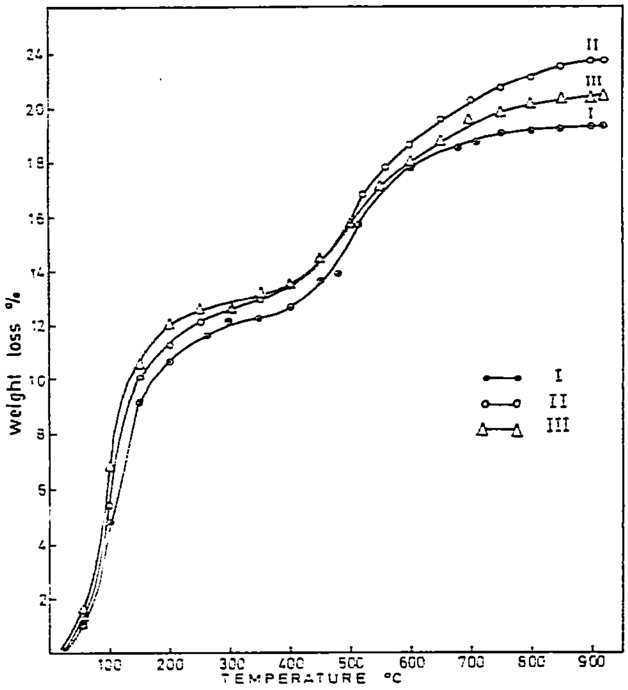

Fig. 2. Thermogravimetric analysis of wadi gharandel clays.

recorded by DTA, perhaps because of its minute amount and the occurence of gypsum endotherms in almost the same temperature range of the clay's first endotherm.

X-Ray diffractometry results of the investigated samples are shown in Fig. 3 from which the interlattice spacings (*d*, Å) and the relative intensities (I/I_0) were calculated. Comparing with the ASTM cards it could be concluded that sample I consists mainly of illite mineral with appreciable amounts of montmorillonite and kaolinite. Quartz and feldspar (most probably orthoclase) show themselves in detectable amounts. Sample II is an admixture of montmorillonite, illite and kaolinite with small amounts of quartz and calcite as well as some gypsum. Sample III consists of illite, montmorillonite and kaolinite. Small amounts of gypsum, quartz and calcite are also present as accessory minerals in this sample. It is observed, however, that gypsum contamination of sample II is much less than that in sample III, while the reverse is true with respect to the calcite content of the two samples. The non-clay minerals of the three samples were also clarified by scanning the coarse fraction (>63 μm) of the water leached samples. The latter study confirms the presence of quartz and feldspar in sample I and gypsum, calcite and minute amounts of feldspar in samples II and III.

Data for the chemical analysis of the tested samples are tabulated in Table 1 from which it is clear that the investigated clays are not in a highly pure state. They contain fluxing oxides varying in the order of I < II < III. Such oxides greatly affect the firing conditions of these samples so it is expected that, for example, sample I resists firing more than samples II and III. The value of Fe_2O_3 is somewhat high in the three samples; different

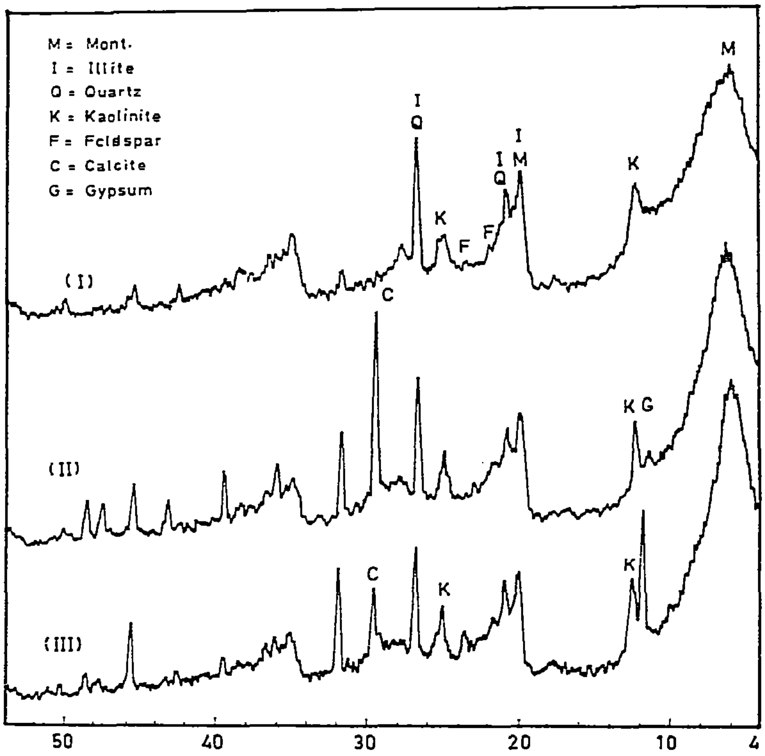

Fig. 3. X-Ray diffractometry of wadi gharandel clays.

grades of brown-reddish colouration are, accordingly, expected in the fired bodies which is an advantage for numerous ceramic products. Sample I shows detectable amounts of MgO while samples II and III show only trace amounts. The higher value for CaO, on the other hand, confirms the previous postulations that samples II and III include calcareous impurities. It has been mentioned that these samples contain various amounts of gypsum and calcite contaminations.

Properties

The physical properties of the fired briquettes are tabulated in Table 2 from which it is clear that good products resulted on firing the prepared

TABLE 1

Chemical analysis of the investigated clay deposits

	I.L. [a]	SiO_2	Fe_2O_3	Al_2O_3 + TiO_2	CaO	MgO	Na_2O	K_2O	total	F.L. [b]
I	19.20	43.87	8.22	21.41	1.80	1.20	3.00	1.78	100.48	16.00
II	21.60	42.00	7.35	19.84	4.26	Traces	3.90	1.61	100.56	17.12
III	20.51	41.02	6.55	20.06	5.80	0.30	4.16	1.71	100.11	18.52

[a] I.L. = Ignition loss.

[b] F.L. = Fluxing oxides = $Na_2O + K_2O + Fe_2O_3 + CaO + MgO$.

TABLE 2

Physical properties of the fired bodies

		Bulk density (gm cm^{-3})	Water absorption (%)	Apparent porosity (%)	Linear shrinkage (%)	Compressive strength (kg cm^{-2})
I	h	2.06	3.51	7.01	20.80	150
	m	2.25	1.87	4.21	17.80	980
II	h	1.61	25.54	40.00	16.60	90
	m	1.79	17.47	29.38	14.60	566
III	h	1.65	21.76	35.34	14.40	120
	m	1.76	17.56	31.16	13.80	694

h = Hand moulded; m = auger machine moulded.

bodies for 1.5 h at 900°C. Sample I bodies show a very low apparent porosity and water absorption, high linear shrinkage and outstanding bulk density and compressive strength. Bodies prepared from samples II and III, however, reveal a moderate bulk density, high apparent porosity, water absorption and compressive strength. Such properties indicate that the fired bodies have reached their firing zone, i.e. we have arrived at the sintering interval where the bodies have been packed well, forming dense bodies with semiclosed pores. This may suggest an earlier formation of the glassy phase in such samples. The glassy phase formation may be enhanced by the presence of appreciable amounts of fluxing oxides (Table 1). An additional factor which accelerated the glassy phase formation is the illitic nature of the studied clays which is a well-known fact mentioned by various investigators [11]. The densification of the bodies is confirmed by the large shrinkage shown by the three samples. It should be noticed, however, that sample I shows the highest density and shrinkage compared with samples II and III. This criterion may indicate a high degree of sintering. Such a case could be visualized in the light of the enrichment of the illite mineral as well as the absence of carbonates (Figs. 2 and 3). Both accelerate the earlier glassy phase formation and the production of dense bodies with the least porosity and highest strength. Samples II and III, on the other hand, demonstrate comparatively moderate porosity, density and strength. This may be related to two main factors: the first is the relative deficiency of illite mineral compared with sample I, and the second is the presence of appreciable amounts of calcium carbonate impurities in both samples [12]. Such a carbonate decomposes with the evolution of carbon dioxide at a temperature just below 900°C which acts to open the structure, forming porous bodies.

Generally speaking, the samples prepared by auger machine extrusion give better results than those made by hand moulding. Such a phenomenon could be visualized in the light of the fact that the pressure used for extrusion arranges the clay particles so as to be well oriented and decreases the intergrain distance, giving a good chance for easier densification.

Comparing with the international specifications, the raw materials studied here could be used satisfactorly for producing good ceramic products. Sample I is considered as an excellent raw material for producing stoneware bodies. Samples II and III are suitable for producing building bricks, ceramic pipes and tiles.

In the light of the above mentioned properties it is recommended that the investigated clays are of good quality and could be used for producing various ceramic products with a pronounced quality. Additional interest should be devoted to these clays to throw more light on their thermochemical behaviour and to find the optimum firing conditions for producing the best products. This will be the subject of another article.

REFERENCE

1 I. Nasr and G.M. Gad, Egypt. J. Chem., 16 (1973) 153.
2 A.A. Kolali and G.M. Gad, Indian Ceram. 17 (1973) 101.
3 W. Machu and K.M. Hanna, J. Chem. U.A.R., 1 (1958) 153.
4 A.T.A. Farag, Ph.D. Thesis, Cairo University, 1977.
5 R.C. Mackenzie, The Differential Thermal Analysis of Clays, The Mineral Society, London, 1957, p. 1.
6 D.N. Todor, Thermal Analysis of Minerals, Abacus Press, Kent, 1976, pp. 210—243.
7 W.G. Bradley, Am. Mineral., 30 (1945) 704.
8 G.M. Gad and M. Abdel Maksoud, J. Chem. U.A.R., 9 (1966) 235.
9 Egyptian Standard Specifications, Ministry of Industry, Ceramic tiles, EOS/293/271/ (1962).
10 A.A. Khalil and G.M. Gad, Build Int. (Engl. Ed.), 5 (1972) 145.
11 P. Weber, Zem. Kalk Gips, 17 (1964) 335.
12 H. Salmang, Ceramics, Springer, Berlin, 4th edn., 1958, p. 179.