A STUDY OF MULTANI MITTI *

AINUL HASAN KHAN

Chemical Research Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

(Received January 30, 1961)

No work has yet been done for the identification of the Khairpur clay, better known as Multani mitti, which is believed to be fuller's earth. The author has investigated the mineralogical composition and tried to estimate the different components in order to facilitate scientific utilisation. The investigations show that Multani Mitti agrees well with Attapulgite Palygorskite, a clay mineral found in fuller's earth from Attapalgus, Georgia etc. The relative percentages of different components have not been determined precisely, but free silica was found to be 2.75% (± 0.25%).

Introduction

There is a vast deposit of clay in Khairpur, which is known as "Multani mitti". This clay is widely used for different purposes, and is generally believed to be fuller's earth. No work has yet been done for its identification, and it was therefore thought worthwhile to study the mineralogical composition and if possible to estimate the different components in order to facilitate its scientific utilization.

Information on the geology of the area is meagre, but from the scanty literature available it may be said that the land is very young geologically, belonging to the tertiary and post-tertiary periods. It is formed by the upheaval of the land from Tethys Sea, which once covered the whole of Western Pakistan, but gradually withdrew with the rising of the Himalayas and its flanks.[1] The sedimentary nature of the clay can be easily recognized by its stratification.

1. Chemical Composition

The chemical composition of the representative specimen is as follows:

SiO_2, 51.50%; Al_2O_3, 19.06%; Fe_2O_3, 7.31%; TiO_2, 1.19%; CaO, 0.39%; MgO, 2.51%; K_2O, 2.60%; Na_2O, 0.99%; loss on ignition, 8.90%.

The silica-alumina ratio is about 3.

2. Identification By X-ray Diffraction

The reference specimen is yellow in colour, apparently amorphous powder. Eighty-four percent of the clay is less than 4 microns, and the pretreatment, using water for separation of clay fraction, was not effective due to very small particle size. It was packed in plastic specimen holder and analysed by X-ray diffractometer (Seifert). The instrumental setting used was as follows:

Counting rate, 3000 counts/second; time constant, 3 seconds; Geiger over-voltage, 1500 volts; divergence slit, 1.5; receiving slit, 4.5; scatter slit, 0.5; scanning speed, 5′/1°; chart scale, 300 mm./h.; radiation Cu. Kα; (15 mA-40 kV).

The principal reflections can be indexed as follows:

10.495 A°	4.49 A°	3.24 A°	2.57 A°
(110)	(040)	(400)	(510)

which corresponds to attapulgite. The diffraction diagram is given in Fig. 1. Quartz, kaolin and limonite are fine grained impurities. Leaching with dilute hydrochloric acid was not effective for the removal of limonite. Digestion of the clay with concentrated hydrochloric acid for 4 hours on water bath removed most of the limonite giving a pale cream product. The structure of attapulgite was resistant to the acid treatment and gave the same reflections except that the quartz reflections were sharper.

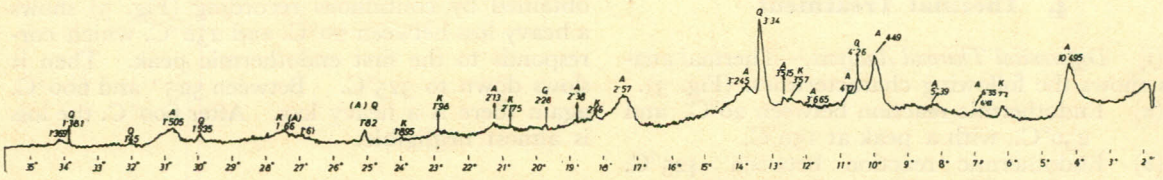

Fig. 1.—X-ray diffraction diagram of Multani mitti.

*The major part of the work described in this communication was carried out at the laboratories of Societe Francaise de Ceramique during the tenure of a French Government Fellowship in the year 1959.

(*i*) *Effects of Treatment with Ethylene Glycol.*—This caused the 10.495 A° reflection to be replaced by one at 10.625 A°. The general nature of other reflections remained the same. The procedure is as follows:the pulverized specimen was treated with drops of ethylene glycol, mixed thoroughly with a glass rod, packed on a plastic holder, then studied by X-ray.

(*ii*) *Effects of Treatment with* NH_4NO_3.—Powdered specimen was boiled in N ammonium nitrate solution for 10 minutes and studied by X-ray. No change was observed.

(*iii*) *Estimation of* SiO_2 *(Free)*.—Estimation of free silica by chemical methods gives disappointing results. The method of Legrand and Nicolas[2] was followed to estimate the quartz content of Multani mitti.

The height of the peak of 25° reflection of quartz was measured (using Al 41° as external standard). This height gave the percentage of quartz from the standard curve. The standard curve was obtained by plotting the relative heights of quartz reflections against the percentage of quartz mixed with illite (attapulgite is more related to illite than any other clay mineral). This method gave the percentage of quartz in Multani mitti as 2.75% (± 0.25%).

3. Electron Micrographic Examination

The elctron microscope has permitted the precise determination of the shape of various clay minerals. A thin membrane of parlodion (2% in amyl acetate) was coated on a grate. Dried by passing infra-red rays. Two mg. of the clay was shaked with 5 ml. of distilled water. One drop of this clay suspension was taken on the grate and dried in the same manner. It was studied under the electronic microscope.

The electronic micrograph of Multani mitti shows single laths and bundle of laths (Fig. 2). There is no evidence of tubular form (like that of halloysite). Small, poorly defined flakes, grouped together in irregular aggregates may be due to the presence of illite. Big hexagonal crystals seem to be that of kaolinite (or may be of quartz).

4. Thermal Treatment

(*i*) *Differential Thermal Analysis.*—Thermal analysis shows the following characteristics. (Fig. 3).

(*a*) Endothermic reaction between 20°C. and 250°C., with a peak at 150°C.

(*b*) Endothermic reaction between 425°C. and 700°C., with a peak at 575°C.

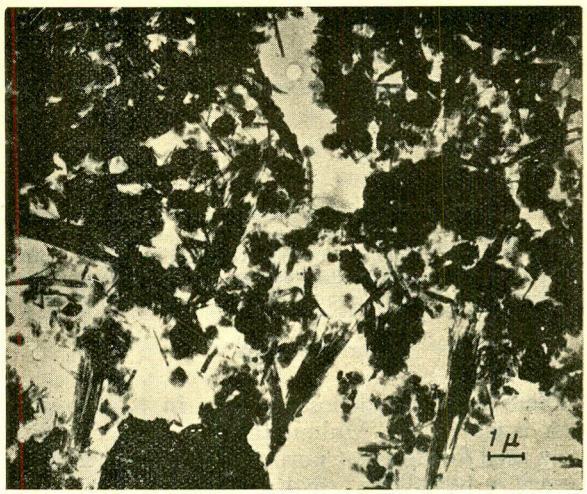

Fig. 2

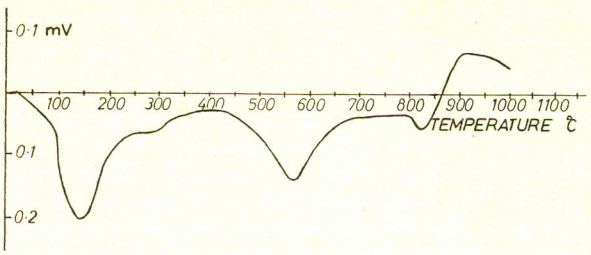

Fig. 3.—Differential thermal analysis curve. Rise of temperature: 400°C./hr.

(*c*) Endothermic reaction between 800°C. and 865°C., with a peak at 830°C.

(*d*) Exothermic reaction starts at 865°C. and peak is attained at 910°C.

When HCl-treated clay was analysed thermally, the general nature of the curve remained the same except slight changes in temperature ranges of endothermic and exothermic peaks. The area of the first endothermic inflection has decreased in comparison to that of the untreated one.

The sample was reheated to study its behaviour. It gave a peculiar curve (Fig. 4).

(*ii*) *Dehydration Curve.*—The weight loss curve obtained by continuous recording (Fig. 5) shows a heavy loss between 20°C. and 250°C. which corresponds to the first endothermic peak. Then it slows down to 325°C. Between 325° and 600°C. again there is a heavy loss. After 600°C. the loss is almost negligible.

(*iii*) *Dilatation Curve.*—The dilatation curve

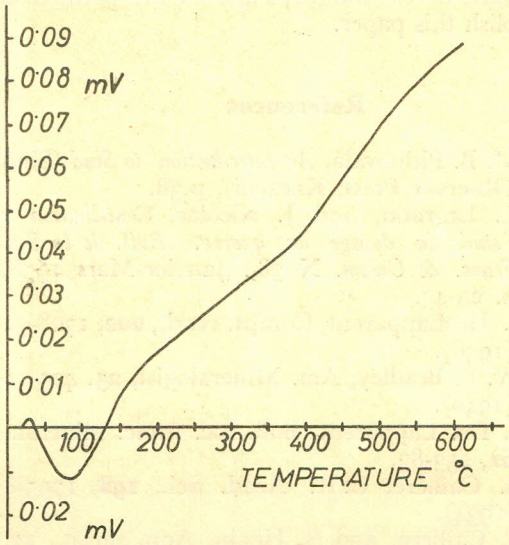

Fig. 4.—Differential thermal analysis curve. Rise of temperature: 4000° C./hr.

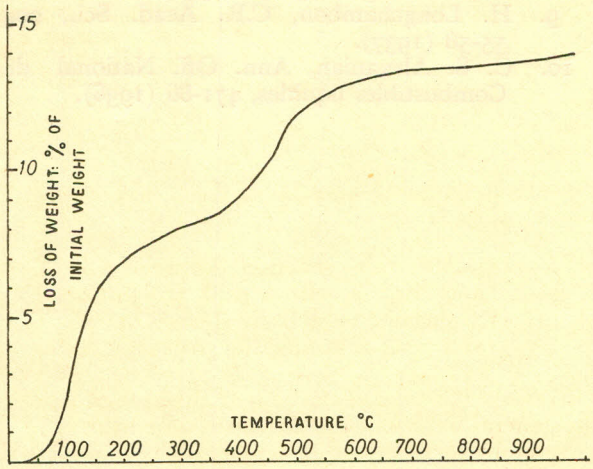

Fig. 5.—Dehydration curve.

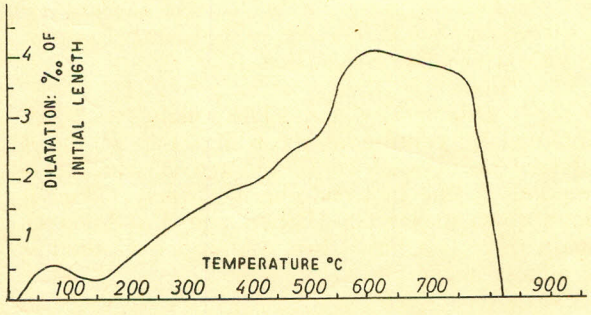

Fig. 6.—Dilatation curve.

shows the following facts (Fig. 6):

(*a*) Slight contraction between 60°C. and 150°C.
(*b*) Slight contraction between 400° C. and 450°C.
(*c*) Slight contraction between 525°C. and 550°C.
(*d*) Maximum expansion (4.25‰ of the initial length) was achieved at 615°C., and then slight contraction continued till 775°C.
(*e*) Large contraction after 775°C.

4. Discussion

In the light of the above obtained X-ray data Multani mitti agrees well with attapulgite-palygorskite first described by De Lapperant.[3] He

Table 1.—Powder Data for Attapulgite (Palygorskite).

	Data by Bradley (1940)							
	Data calculted from proposed structure		Experimental data		Experimental data by Lapparent		Multani mitti	
hkl	d	I	d	I	d	I	d	I
110	10.48	330	10.50	10	10.2	12	10.495	70
200	6.45	17	6.44	6	6.44	2	6.45	6
130	5.44	12	5.42	5	5.3	2	5.44	10
220	5.24	1						
040	4.50	66	4.49	8			4.49	100
310	4.18	13	4.18	3	4.3	10	4.17	25
240	3.69	18	3.69	5				
330	3.49	12	3.50	3			3.52	15
150	3.47	2						
400	3.23	120	3.23	10	3.25	10	3.25	40
420	3.04	3	3.03	1				
350	2.76	2						
440	2.62	43	2.61	8				
510	2.56	8	2.55	3	2.55	10	2.58	60
530	2.38	5	2.38	3			2.38	13
080	2.25	1						
600	2.15	15	2.15	5	2.25	4	2.13	13
550	2.10	1						
480	1.845	1						
390	1.815	3	1.82	1	1.80	2	1.82[q]	13
660	1.75	1						
800	1.615	3	1.62	1	1.67	2	1.66[k]	17
680	1.555	17	1.56	3				
0120	1.50	40	1.50	5	1.49	4	1.50	30

d: spacing I: intensity, q: attapulgite masked by quartz, k: attapulgite masked by kaolin.

found this clay mineral in fuller's earth from Attapulgus, Georgia, Quincy, Florida and Mormoiron (France). Bradley[4] has determined the structure of the mineral, showing silica chain similar to those in amphibole to be essential components of its structure. Bradley[4] gives the ideal formula of attapulgit[4] as $(OH_2)_4$ $(OH)_2$-Mg_5 Si_8 O_{20}. $4H_2O$ in which there is a considerable replacement of Mg by Al.

The X-ray data obtained by the author, by De Lapparent[5] and by Bradley are collected and compared in Table 1.

The electron micrograph clearly confirms the attapulgite nature of clay. But illite as an impurity cannot be ruled out. Nothing can be said about the relative percentage of different component except that of free silica which was found to be 2.75% (± 0.25%).

The general shape of the curves obtained by differential thermal analysis, dehydration analysis and dilatation also agrees with those of attapulgite obtained by Caillere,[6] Caillere and Henin,[7] De Lapparent,[3] Longchambon[8,9] and Alexanian.[10]

Acknowledgements.—The author is grateful to Mr. Paul Paquin, Directeur Generale, Societe Francsaise de Ceramique, Paris for his permission to publish this paper.

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