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MINERALOGY AND CHEMISTRY OF CLAYS FROM KHAIRPUR, SIND PROVINCE

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The present paper reports on the mineralogy and chemistry of clays collected from Ubban Shah and Allahjoria west mines of Khairpur area. Chemical, x-ray powder diffraction, differential thermal analysis and thermogravimetric analysis suggest that the samples are illite interstratified with some montmorillonite. Quartz, gypsum and some kaolinite are found in subordinate amounts. The clays are not suitable for commercial activation and utilization for the bleaching of oils.

INTRODUCTION

A thick bed of clays runs for about twelve km along the base of a scarp formed by the Eocene rocks in the Shadi Shahid Hills, about 5 km east of Khairpur in Sind Province. (Fig. 1). It formed by the uplift of the land from Tethys sea, which once covered the whole of Pakistan, but gradually withdrew with the rising of the Himalyas orogenic system [1]. The clay is widely used for different purposes, and is generally believed to be fuller's earth. It is known as "Multani Mitti" or "Gile-Multani". Khan [2] reported the mineralogy of clay based on one sample and that of uncertain location. He interpreted the clay as belonging to the Attapulgit-Palygorskite group of minerals.

The present paper reports the mineralogy and chemistry of clays and associated samples collected from Ubban Shah and Allahjoria west mines. All samples are yellow in colour. The details of each sample are as follows:

- KH1 Limestone, top of clay
- KH2 Ubban Shah Mine, top zone
- KH3 Ubban Shah Mine, middle zone
- KH4 Ubban Shah Mine, lower zone
- KH5 Ubban Shah old dump sample
- KH6 Allahjoria West (Mine 2).

MINERALOGICAL INVESTIGATIONS

1. *X-ray Diffraction.* The X-ray powder diffraction data of all the six samples are given in Table 1. Small amount of specimen powder was mixed with two drops of Collodion; it was moulded into a thin rod about 1/2 mm dia and 1 cm in length by rolling between two glass slides. Debye-Scherrer Camera (114.6 mm dia) was used. The specimens were exposed to $\text{CuK}\alpha$ radiation for seven hours with 35 KV

and 18 mA.

The Principal reflections of the clays can be indexed as:

10.40	4.50	3.36	2.58
001	120;110	022;003	200;131

which corresponds to illite except that 001 is higher by 0.40\AA . Ethylene glycol treatment shifts 10.40\AA reflection to 10.60\AA . X-ray diffraction patterns are unaffected by heating to 350° .

However, when the samples are heated to 600° most of the reflection become faint. It is concluded that the clay mineral is illite-montmorillonite mixed-layer type which is designated as "IM".

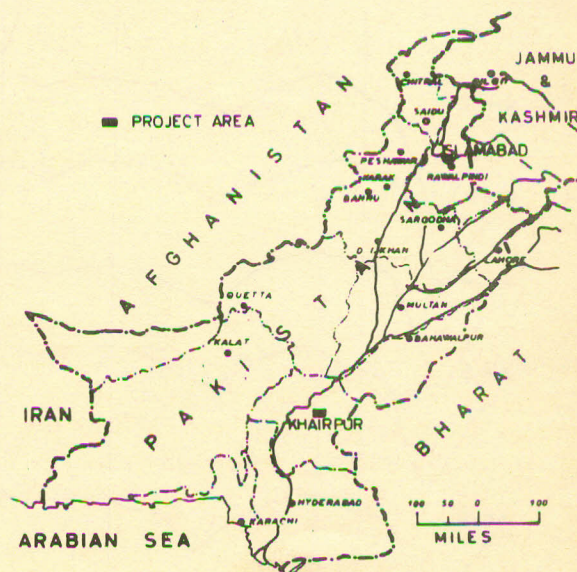


Fig. 1. Map of Pakistan.

From the X-ray data the following conclusions regarding the mineralogy may be made:

KH1	Calcite, IM
KH2	IM, quartz, gypsum
KH3	IM, quartz, Kaolin
KH4	IM, quartz, Kaolin
KH5	IM, and quartz
KH6	IM, quartz, Kaolin

The Table 2 gives the X-ray diffraction data of the residue of KH1 left after treatment with acetic acid(a) and hydrochloric acid(b) and the heavy mineral separated from the acid residue(c). Again the following conclusions regarding the mineralogy may be made:

KH1(a)	IM, quartz and dolomite
KH1(b)	IM, and quartz
KH1(c)	Olivine

2. *Differential Thermal Analysis.* The DTA curves of all the six samples are given in Fig. 2. The DTA curve of KH1 contains the typical peak of calcite (950°) with a tiny peak of dolomite (810°). The thermal curves of other samples are very similar to each other with the following characteristics:

a) Endothermic reaction between 60° and 340° with a peak at about 160°.

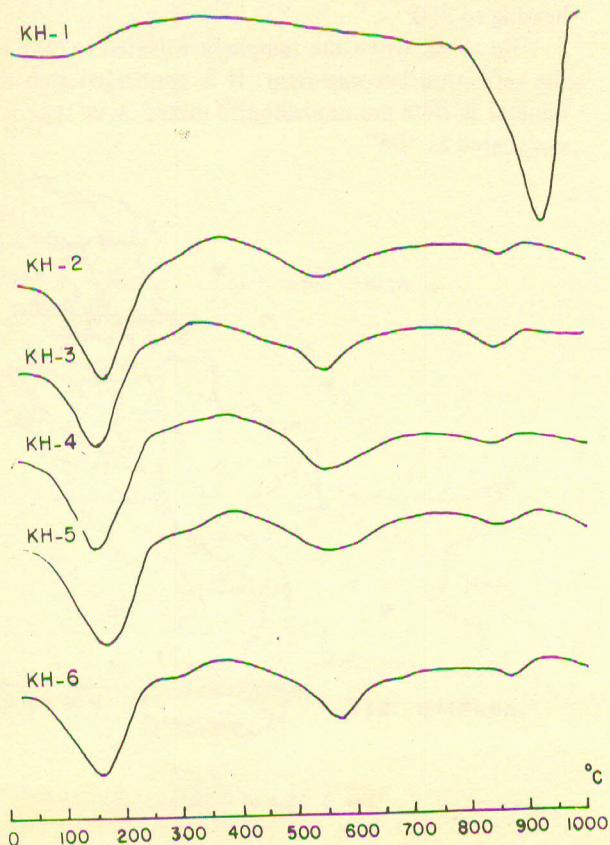


Fig. 2. Data curves.

b) Endothermic reaction between 340° and 620° with a peak at about 580°.

c) Endothermic reaction between 800° and 880° with a peak at about 850°.

3. *Thermogravimetric Analysis.* The weight-loss curves obtained by continuous recording (Fig. 3) of the clay samples are very similar to each other. The curve shows a heavy loss between 60° and 340° which corresponds to the first endothermic peak. Between 340° and 620° again there is loss corresponding to the 2nd endothermic peak. After 620° there is a slight gain in weight, most probably due to the oxidation of ferrous iron.

CHEMICAL INVESTIGATIONS

Chemical Compositions. The results of the chemical analysis of six samples are given in Table 3.

The sample KH1 being a limestone contains a high percentage of lime and CO₂. The MgO content (1.60) is due to the presence of dolomite. As this sample is free of

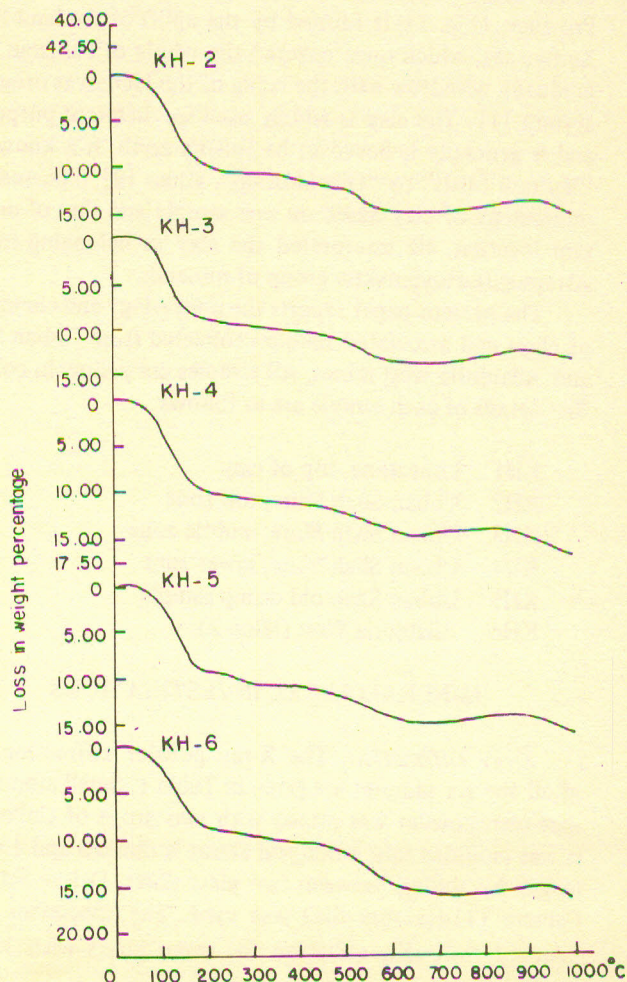


Fig. 3. TG curves.

Table 1. X-ray powder diffraction data.

KH1			KH2			KH3			KH4			KH5			KH6		
dA°	I		dA°	I		dA°	I		dA°	I		dA°	I		dA°	I	
10.48	1	IM	10.48	30	IM	10.40	30	IM	10.40	15	IM	10.40	70	IM	10.40	10	IM
3.82	10	C	7.56	15	g	7.13	2	k	7.13	5	k	4.52	30	I	7.13	10	k
3.02	100	C	4.55	50	I	4.50	40	I	4.49	20	I	4.24	10	q	4.95	1	I
2.89	2	C	4.23	50	q	4.23	20	q	4.23	5	q	3.49	1	I	4.49	70	I
2.49	20	C	3.36	100	q	3.56	2	I	3.52	1	I	3.36	100	q	4.25	60	q
2.28	25	C	3.18	1	I	3.35	100	q	3.35	100	q	3.24	1	—	3.56	10	I
2.08	25	C	3.07	10	I	2.57	40	I	2.57	30	I	2.58	20	I	3.35	100	q
1.90	30	C	2.88	8	—	2.46	3	I	2.46	5	I	2.45	2	I	3.07	1	I
1.86	30	C	2.67	2	—	2.39	½	I	2.12	1	q	2.13	½	q	3.07	1	k
1.59	10	C	2.59	30	I	2.26	1	q	1.91	1	k	2.04	½	k	2.89	30	—
1.51	10	C	2.46	2	I	2.12	1	q	1.81	2	I	1.98	½	I	2.58	20	I
1.47	1	C	2.39	1	I	1.98	2	q	1.53	2	q	1.90	½	I	2.46	15	I
1.43	10	C	1.99	1	I	1.90	10		1.49	3	I	1.82	5	I	2.29	3	q
1.41	5	C	1.89	1	I	1.82	5	I	1.43	10	—	1.66	1	I	2.23	2	q
			1.82	5	I	1.69	½	I				1.50	2	I	2.20	2	q
			1.66	1	I	1.65	1	I				1.37	2	q	2.12	10	q
			1.55	½	q	1.54	10	q							1.99	½	I
			1.50	2	I	1.50	15	I							1.82	20	I
						1.37	10	K							1.67	10	I
															1.54	20	I
															1.37	15	k
															1.30	2	k
															1.25	2	k

I = illite; K = Kaolinite; C = calcite; IM = mixed layer; g = gypsum; q = quartz

Table 2. X-ray powder data for residue of KH1.

KH1 (a)			KH1 (b)			KH1 (c)		
dA°	I		dA°	I		dA°	I	
10.40	10	IM	10.28	60	IM	4.72	10	O
4.47	10	I	6.32	6	I	3.31	5	O
4.21	10	q	4.48	60	I	2.92	10	O
3.70	5	d	4.23	50	q	2.48	100	O
3.35	50	q	3.36	100	q	2.06	60	O
2.91	100	d	3.19	3	I	1.59	70	O
2.79	1	—	2.58	30	I	1.46	90	O
2.68	8	d	2.49	10	q			
2.56	4	d	2.28	5	q			
2.51	½	d	2.12	20	q			
2.41	4	d	1.82	40	q			
2.20	30	d	1.66	20	q			
2.01	30	d	1.60	5	q			
1.80	40	d	1.54	15	q			

(continued. . .)

(Table 2, continued . . .)

1.50	5	I	1.50	15	I
1.46	10	d	1.46	5	q
			1.38	20	q
			1.29	5	q
			1.25	2	q
			1.20	5	q
			1.18	5	q
			1.15	2	q

IM = mixed layer; I = illite; q = quartz; d = dolomite; O = olivine

Table 3. Chemical analysis of Khairpur clays.

% Composition	KH1	KH2	KH3	KH4	KH5	KH6
SiO ₂	2.60	45.70	48.60	50.22	46.80	46.20
Al ₂ O ₃	5.00	24.29	23.38	22.85	24.61	22.86
TiO ₂	0.00	0.71	0.77	0.77	0.75	0.71
Fe ₂ O ₃	0.91	7.56	6.55	7.21	7.59	8.06
FeO	0.26	0.38	0.38	0.44	0.26	0.64
CaO	48.54	1.19	1.40	Traces	0.60	2.43
MgO	1.60	1.86	2.16	1.58	2.96	1.94
Na ₂ O	0.32	2.12	2.31	2.12	2.18	1.25
K ₂ O	0.10	3.12	3.12	3.18	2.87	2.62
MnO	0.04	0.08	0.04	0.04	0.06	0.07
P ₂ O ₅	0.00	0.04	0.04	0.04	0.00	0.00
SO ₃	—	0.64	0.25	0.44	1.10	0.32
H ₂ O ⁻	—	2.65	1.62	1.45	3.23	2.28
H ₂ O ⁺	—	10.55	9.84	10.77	7.71	10.37
CO ₂	40.44	0.00	0.00	0.00	0.00	0.00
Total :	99.81	100.89	100.46	101.11	100.72	99.75
pH	8.34	7.45	8.90	8.65	8.34	9.40
Colour	Light Yellow	Yellow	Yellow	Yellow	Yellow	Yellow

quartz the silica (2.60 %) and alumina (5.00 %) seem to be located in the clay minerals.

The chemical composition of the clay samples is similar to those of Illite except that K₂O content is low, Na₂O and H₂O are high. The higher amount of H₂O and lower amount of K₂O suggest that montmorillonite may be present. Fe₂O₃ content of clays varies between 6.55 and 8.06. As the colour of the clays are yellow, the iron may be present as hydrated iron oxide-limonite.

Cation Exchange Capacity. The cation exchange capacity of a composite clay sample is about 48 milli-equivalent per 100 g. The cation exchange capacity of a normal illite is about 35 m. Thus the slightly higher C.E.C. of the Khairpur clays also indicated the presence of some montmorillonite.

Activation Tests. The aim of activation test is to find a suitable use of the extensive deposits. Activated clays are used for bleaching of oils-vegetable as well as petroleum

products. In order to assess the suitability of the clays, a composite sample was powdered to pass 85 BSS mesh 50 g of the sample was refluxed with 100 ml of H_2SO_4 (4N) for 4 hours. When cold it was filtered and washed with hot distilled water, till free of $-SO_4$ ions. The sample was dried and powdered to pass 300 BSS sieve. 1 g of the sample absorbed about 45 mg of methylene blue, whereas imported German Terrana absorbs about 110 mg of methylene blue.

DISCUSSION

In the light of the above X-ray diffraction, DTA, TGA and chemical data the previous conclusion of Khan [2] that the Khairpur clays are composed of attapulgite-palygorskite group of clay minerals is questionable. The clay minerals seem to be illite with some interstratification with montmorillonite. The proportion of montmorillonite seems to be lower than 20 % in the illite structure [3].

Quartz, gypsum and some kaolinites are found in subordinate amounts. Vertical as well as lateral variation in the composition of Ubban Shah Clays (KH2 to KH5) and Allahjoria (KH6) is not evident; which indicates uniformity in the mineral composition. The high pH of the clays

(determined by an aqueous suspension of the ground material) may be equated approximately with that of the waters of the depositional environment [4,5]. Such a high pH indicates that an alkaline lake might have been the basin of deposition.

Presence of yellow iron oxides and absence of organic matter suggest that the chemical environment was oxidising (+Eh). Thus it may be concluded that the sediments were deposited in shallow and turbulent water.

The low cation exchange capacity of the clay together with lower methylene blue adsorption of the clay show that the material is not suitable for commercial activation and utilization for the bleaching of oils etc.

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