

PHYSICO-CHEMICAL PROPERTIES OF SOME INDIGENOUS CLAYS

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Chemical composition, X-ray powder diffraction, simultaneous DTA and TGA and activation studies of clay samples collected from D.G. Khan, Dherikot (Attock) and Khairpur are being presented. The clays from D.G. Khan and Dherikot after activation may be utilized for bleaching purposes, whereas the Khairpur clays are not suitable for commercial activation and utilization for the bleaching of oils.

Key words: Clay, activation, bleaching.

INTRODUCTION

Clays activated by chemical treatment are extensively employed in refining and bleaching mineral and vegetable oil [1]. Clays belonging to the bentonite group make highly efficient adsorbents because of their high base exchange capacity. Bentonite is a very fine grained rock containing more than 80 % of clay mineral montmorillonite (Mg,Ca) $\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5 \text{SiO}_2 \cdot \text{H}_2\text{O}$.

There are two major types of bleaching clays: Fuller's earth and acid-activated clays. Fuller's earth is naturally active and ordinarily does not respond satisfactorily to acid activation but on the contrary acid-activated clay is of bentonitic origin and has very low natural activity but respond favourably to acid activation.

A considerable quantity of indigenous bentonite is estimated to be available. Ali [2] has reported bentonite deposits in the Punjab and Azad Kashmir. Deposits of bentonite clays have also been reported in D.G. Khan [3], Dherikot (Attock) [4] and Khairpur [5].

At present the requirements of Fuller's earth for bleaching edible oil are almost entirely met by imports from different countries which increase the cost of finished products. With a view to meeting the requirements of bentonite in our industries, acid activation studies on the above clays were undertaken.

EXPERIMENTAL

Chemical analysis. 100 g of the samples were ground to a fine powder (-10 +120 mesh) and analysed using standard methods of chemical analysis [6]. The constituents determined were SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , MgO , Na_2O and K_2O . The results of the analyses are summarised in Table 1.

X-Ray powder diffraction. X-Ray studies were made on the natural samples, clays obtained after washing the samples and on ethylene glycol treated clays. Small amount of ethylene glycol was mixed with sample and then it was subjected to the X-ray studies. Glycolation [7] of the samples enhanced the 001 spacing from 13.25 Å to 15.23 Å confirming the presence of montmorillonite in the samples. The three strongest lines with relative intensities of the minerals, identified are presented in Table 2. Debye-Scherrer camera (114mm dia.) was used and the specimen was exposed to Ni-filtered Cu-radiation for 6 hr. at 35 KV and 18 mA.

Simultaneous DTA and TGA. Simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) were carried out on MOM derivatograph.

Sample (1.25 g) in a platinum crucible was subjected to heat in an electric furnace. Al_2O_3 (1.25g) in a similar crucible was used as reference material. Simultaneous DTA and TG were recorded on photographic chart. The thermograms are shown in Fig. 1.

Table 1. Chemical analysis of clay samples

Percent composition	D. G. Khan				Dheri-	Khair-
	1	2	3	4	kot- 5	pur 6
SiO_2	49.60	46.80	47.07	46.80	53.23	46.20
Fe_2O_3	6.66	8.13	6.30	6.60	2.70	8.76
Al_2O_3	11.94	12.46	12.45	12.83	15.48	22.86
CaO	9.12	8.84	11.31	10.52	2.92	2.43
MgO	3.18	2.87	3.11	3.04	1.02	1.94
Na_2O	0.25	1.12	0.68	0.33	5.90	1.25
K_2O	1.94	2.01	1.91	2.02	2.20	2.62
L.O. Ign.	16.18	16.60	16.20	16.65	16.89	12.65
Total	98.87	98.83	99.03	98.07	100.34	98.71

Table 2. X-ray diffraction data of clay samples.

	D.G. Khan						Dherikot (Attock)						Khairpur					
	Unwashed		Washed		E.G.		Unwashed		Washed		E.G.		Unwashed		Washed		E.G.	
	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
Montmorillonite	13.25	30	13.25	100	16.23	60	15.25	100	15.24	100	16.00	100	—	—	ND	—	—	ND
	4.52	20	4.52	40	4.50	40	4.46	85	4.42	100	4.43	70	—	—	ND	—	—	ND
	2.56	20	2.56	30	2.50	30	2.55	60	2.54	70	2.53	50	—	—	ND	—	—	ND
Illite	9.85	5	9.85	—	9.85	—	—	—	—	—	—	—	10.40	70	ND	—	—	ND
	4.48	3	4.48	—	4.48	—	—	—	—	—	—	—	4.49	20	ND	—	—	ND
	3.36	—	3.34	—	3.35	—	—	—	—	—	—	—	3.35	100	ND	—	—	ND
Kaolinite	7.08	8	7.08	10	7.08	10	—	—	—	—	—	—	7.13	5	ND	—	—	ND
	3.58	6	3.57	5	—	—	—	—	—	—	—	—	3.56	2	ND	—	—	ND
	1.49	7	1.49	5	1.49	5	—	—	—	—	—	—	1.49	1	ND	—	—	ND
Quartz	3.36	100	—	—	—	—	3.33	100	—	—	—	—	3.35	50	ND	—	—	ND
	4.23	35	—	—	—	—	4.25	85	—	—	—	—	4.24	30	ND	—	—	ND
	1.80	20	—	—	—	—	1.81	30	—	—	—	—	1.80	10	ND	—	—	ND
Calcite	3.02	50	3.02	30	3.02	20	—	—	—	—	—	—	—	—	ND	—	—	ND
	2.27	7	2.27	5	2.27	5	—	—	—	—	—	—	—	—	ND	—	—	ND
	2.10	4	—	—	2.10	1	—	—	—	—	—	—	—	—	ND	—	—	ND
Gypsum	—	—	—	—	—	—	—	—	—	—	—	—	7.56	15	ND	—	—	ND
	—	—	—	—	—	—	—	—	—	—	—	—	4.25	10	ND	—	—	ND
	—	—	—	—	—	—	—	—	—	—	—	—	3.07	—	ND	—	—	ND

ND = Not Determined.

Table 3. Swelling index, C.E.C. and methylene blue adsorption activity.

S. No.	Locality	Swelling index percent	C.E.C. m.eq/100 g clay	Methylene blue adsorption by 1 g activated clay mg
1.	D.G. Khan	25	20	68
2.	Dherikot	30	35	80
3.	Khairpur	10	46	45

Activation process. The process of activation consists in leaching the clay with a suitable concentration of acid and heating for a pre-determined time. Cation exchange [8] takes place during the process of acid leaching. The bond energy [3] of the clay molecule is modified in such a

way that the surface energy of the clay is sharply enhanced. The acid (sulphuric) concentration and leaching time interval were varied in order to find out the optimum acid concentration and time interval for activation. Maximum activation was achieved when the acid strength and the time interval were 4N and 3hr respectively. The acid activated clays were washed with distilled water to remove all the free acid, and after drying they were tested for bleaching activity with a methylene blue standard solution. When the activated clay was mixed with a methylene blue solution, the colouring matter was adsorbed on the surface of the clay particles and colourless liquid was obtained on filtration.

Methylene Blue Test

Preparation of methylene blue dye. 1 g crystalline methylene blue was dissolved in 250 ml of warm distilled

water and diluted to 1 litre. The solution contained 1 mg methylene blue per ml.

Bleaching test with methylene blue solution. 1 g clay sample was taken in a 250 ml beaker. Methylene blue solution was added from a 50 ml burette, 2 ml at a time. Immediately after adding the dye the contents of the flask were swirled and a small portion of the suspension was spotted on the filter paper (Whatman No. 41) by means of a glass rod. Whilst the dye was being adsorbed by the clay, there was a sharp boundary on the filter paper between the blue clay/dye spot and the water which was radiated from the spot. As the end point reached a light blue halo was formed around the spot by excess of the dye. The suspension was allowed to stand for 2-5 min. without further addition of the dye. More dye was added on the disappearance of the blue halo but if it persisted, the suspension was allowed to stand for 20 min. longer. After this period the persistence of halo indicated the end point. The results are reported as methylene blue adsorbed per g of clay sample in Table 3.

Determination of cation exchange capacity. For the determination of cation exchange capacity (C.E.C.) the above mentioned method, with the only exception that the crystalline methylene blue dye was dried at 105° before dissolving 3 g per litre in distilled water, was adopted. The weight loss of methylene blue at 105° was 12.34%.

As the equivalent weight of anhydrous dye is 319.9 the normality of the methylene blue solution is

$$\frac{3}{319.9} \times \frac{100.00 - 12.34}{100} = 0.0082 \text{ N}$$

The C.E.C. in milliequivalent per 100 g dried (at 105°) clay is calculated from the formula:

$$\text{C.E.C.} = \frac{100 \times \text{volume of methylene blue dye used} \times 0.0082}{\text{weight of dried clay at } 105^\circ}$$

The C.E.C. (m.eq/100 g) of clays are reported in Table 3.

Swelling characteristic. Bentonite clays are characterized [9] by their ability to swell when immersed in water and show swelling properties from 1 to 15 times the volume of the dry material. When saturated clay forms a gelatinous mass and remains in suspension for weeks before settling. Swelling property is one of the reliable tests to identify bentonite. The swelling index values of the samples were determined by adding 10 cm of dry material (-30 +51 mesh) to a graduated cylinder containing 100 ml of water

and measuring apparent volume of settled clay after 68 hr. (Table 3).

RESULTS AND DISCUSSION

The chemical composition reveals that D.G. Khan and Khairpur clays are aluminous and ferrogenous, whereas the Dherikot clay is aluminous only. Moreover, D.G. Khan clay is richer in calcium oxide and magnesia than the Dherikot and Khairpur clays. The alkali contents are the highest in Dherikot clay.

The minerals identified from X-ray powder data of D.G. Khan sample are montmorillonite, illite, kaolinite, quartz and calcite. The reflection $d=13.25 \text{ \AA}$ of the sample after ethylene glycol treatment increased to $d=15.23 \text{ \AA}$, confirming the presence of montmorillonite. Dherikot clay is composed of montmorillonite with subordinate amount of quartz. The reflection 15.24 \AA after glycolation enhanced to 16.00 \AA . X-ray powder data of Khairpur clay indicate that the sample is composed of illite, kaolinite, quartz and gypsum.

The DTA curve (Fig 1a) of D.G. Khan clay shows endothermic peaks at about 140, 580 and 860°. The peak at 860° indicates the presence of calcite. At this temperature calcite is decomposed with the liberation of carbon dioxide. The clay contains illite, montmorillonite and calcite. The TG curve shows losses of 6, 8, and 15% during 60-200°, 500-650°, and 800-900° respectively. The maximum loss is due to the evolution of carbon dioxide.

The DTA curve (Fig. 1b) of Dherikot clay sample shows endothermic peaks at 132°, 650°, and 870°. The clay seems to be montmorillonite. TG curve shows losses

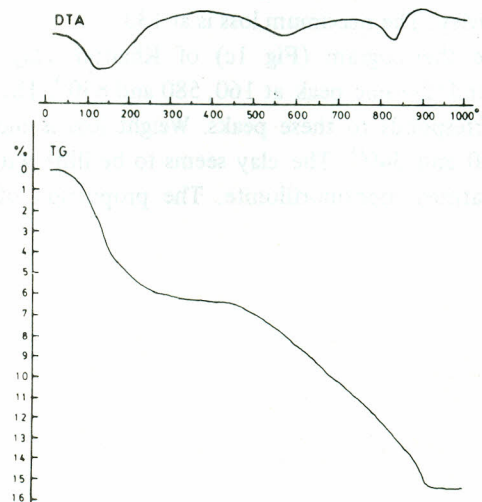


Fig. 1(a)

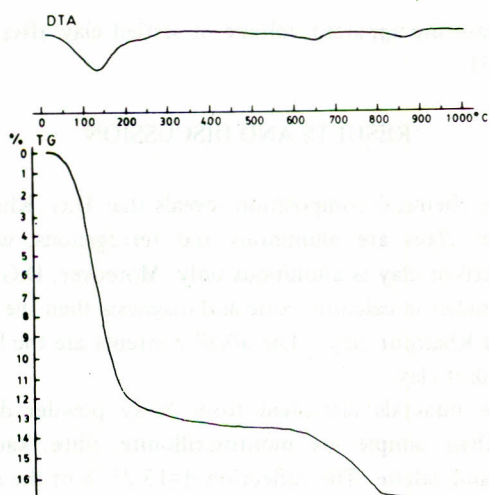


Fig. 1(b)

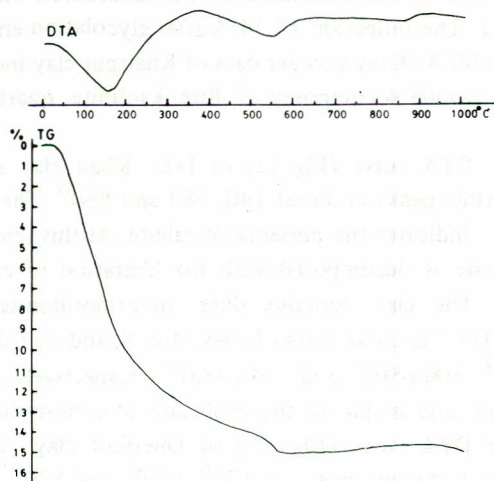


Fig. 1(c)

of 13, 14 and 16% during 50–200, 600 and 800–900°C respectively. The maximum loss is at 130°C.

The thermogram (Fig 1c) of Khairpur clay sample shows endothermic peak at 160, 580 and 850°C. The weight loss corresponds to these peaks. Weight loss is more between 60 and 340°C. The clay seems to be illite with some interstratified montmorillonite. The proportion of mont-

morillonite is lower than 20% in the illite structure (10).

The acid activation of indigenous clays reveals that D.G. Khan and Dherikot clays after treatment with 4N sulphuric acid for 3 hr may be employed for bleaching purposes. However, before activation these clays have to be beneficiated. The economics of the activation process depends upon the loss of clays during elutriation process, acid consumption and reuse of the acid employed for activation as well as the cost of drying of the activated clays. Khairpur clays have low refining activity and cannot be used for the bleaching of oils.

Bentonite clays are generally evaluated on the basis of moisture content, particle size and amount of grit, C.E.C. and swelling property.

A systematic survey of the indigenous bentonite deposits and their acid activation studies is recommended.

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