

CHARACTERISATION OF FULLER'S EARTH FROM D.G. KHAN

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Fuller's earth from D.G. Khan has been studied with an aim of its characterisation and evaluation as a bleaching earth. Its mineralogy, cation exchange capacity, swelling index, D.T.A. chemical analysis, surface area, activation and bleaching behaviour have been studied and it has been found that this earth, when properly activated, can match the best bleaching earth available in the international market.

Key words: Fuller's earth, Bleaching earth, Chemical analysis.

Introduction

The use of Fuller's earth and bentonite has long been known. There is a growing demand for such argillaceous materials particularly in vegetable and mineral oil refining. Fuller's earth is a variety of clay which in its natural form has the power to decolourise oils, fats and greases [1,2]. The name has no geological significance [3], but owes its origin to the use of certain types of adsorbent clays [4] in the archaic procedure of scouring or fulling wool.

Fuller's earth/bentonite deposits have been found at many places in Pakistan. Reasonably big deposits have been found in Dera Ghazi Khan and Campbellpur (Punjab) Kirk (NWFP) and Mirpur (Azad Kashmir). There are several minor occurrences at other places also. The biggest deposit is that of Dera Ghazi Khan and has been investigated to a greater extent as compared to other deposits. According to surveys carried out by PUNJMIN [5], the Fuller's earth deposit is situated in area between longitudes 70° 9'E to 70° 32'E and 30° -8'N to 30° -45'N latitudes. Fuller's earth is well distributed within Juxtaposed Ghaziji formation and Drazinda Shale member of Eocene era with thin Pinkish limestone and Sirki member imparting boundary between the two formations. The clay horizon extends for most of the extent of Zindapir structure, acquiring appreciable distribution in Safad Koh, Rodo and Dalana areas following close repetition of these beds. Fuller's earth occurs in the form of sand-witched beds within the shales and ranges in thickness from 0.25 to more than 5 meters.

The eastern limb of the deposit has an inferred quantity of 22.5 million tons of clay. Reserves within the western limb and Drazinda shale are equally appreciable.

In this study the Fuller's earth from D.G. Khan has been investigated with an aim of finding out a suitable method for its activation as a bleaching earth. One hundred and forty samples from different locations were studied. Pakistan, at present, is importing a large quantity of bleaching earth from Germany, England, Japan and China. The consumption of bleaching earth by Ghee Corporation of Pakistan and the

Ghee Mills and Cooking Oil Mills in private sector is over 5000 tons per annum. This amounts to a foreign exchange of Rs. 4,50,000 at least. In view of these facts it is clear that this is an important work from the national point of view.

Experimental

Numbering of samples. Samples have been numbered according to the following scheme. The letters refer to different areas.

Rodo area	-	A	The deposit lie North West of Taunsa town and are approachable kot Qaisrani-Rodo track.
by Taunsa-Sanghar	-	S	The deposit is approachable by Taunsa-Kot Qaisrani-Rodo track.
Safed Koh	-	E	The deposit can be reached through Chowkiwala Bharti road, separating from main high way 11 km south of Taunsa.
Basti Taraki	-	K	The same comments as above.
Dahar		F and	Deposit can be reached by Sori.
Nalani		FE-BN I	Nadi. This area is 18-20 km west of Shaden Lund Railway Station.
Dalana	Daa/Dbb		Dalana deposits are close to Dalana village, 15 km south west of D.G. Khan and are easily accessible through D.G. Khan-Daland unmetalled road.
Rakhi-Gaj	-	RA	The deposits are situated close to Rakhi Gaj, 55 km south of D.G. Khan along D.G. Khan Fort Munro Road.

Cation exchange capacity (C.E.C.). Cation exchange capacity was determined by a standard procedure [6] by converting the earth to NH_4 -clay and then replacing NH_4 by K^+ ions. The released NH_4 ions were determined and the C.E.C. was reported as milliequivalents per 100 grams of clay.

Swelling index. Swelling index was determined by taking

10 gms of earth (-100 mesh) dried at 110° into a tall glass tube of 2 cm internal diameter and calibrated in mili litres. The tube was tapped gently and the volume of earth was noted. The tube was filled with distilled water and shaken thoroughly to wet the earth. It was allowed to stand and the volume of the expanded clay was noted after 24 hrs. The swelling index was calculated as the ratio between the expanded volume and the initial volume of the clay.

Surface area. Particle size distribution of the sample was determined by the hydrometer method [7] and the surface area was calculated from the grain size distribution. The values are presented in Table-1.

TABLE 1.

Sample No.	Surface area sq.cm.gm
Daa-3	40158
F-12	42848
A-7	38189
RA1	31568

Differential thermal analysis. DTA was carried out with the help of an Hungarian Derivatograph. The reference material used was calcined alumina (Al₂O₃). Heating rate was 10°/min and the temperature range was from room temperature to 1000°. The samples were ground to 100 mesh for this test.

Infra red analysis. Infra-red analysis of washed clay as well as that of activated clay was carried out. The sample was prepared by wet grinding in an agate mortar to a very fine state. The sample was mounted on sodium chloride pellet with the help of isopropyl alcohol.

X-ray analysis. X-ray diffraction analysis of washed as well as activated clay was carried out with the help of Dabys Scherrer camera, using CuK_α radiation. The exposure time was six hrs. Intensities were determined visually.

Chemical analysis. Chemical analysis was carried out according to standard silicate analysis procedures [8].

Activation by heating. Various samples were heated at 110°, 210°, 500°, 600° and 700° for three hrs. and their bleaching capacity was determined.

Acid activation. The washed clay samples were activated by refluxing with HCl of various strengths for different durations and using various solid-liquid ratios.

In case of activation with H₂SO₄ the heating was done with steam instead of refluxing the mixture.

After acid treatment the clay was washed free of acid with water. The clay was dried at 110° and ground to -200 mesh in an agate mortar.

Testing of bleaching activity. 1.5 gms. of activated clay was added to 100 gms. of dried and neutralized oil and the oil was heated between 90-100° for half an hour with continuous stirring. The clay was filtered out of oil and decolourisation

was measured by tintometer as well as by a spectrophotometer. In case of tintometer the units of yellow and red pigments for unbleached oil were taken as 100% colour for the sake of calculations. In case of spectrophotometer a wavelength was selected at which the oil sample had maximum absorption and minimum transmission in unbleached state. This reading for absorption say χ was considered to be 100% colour and the decolourisation was calculated as follows:

$$\% \text{ Decolorisation: } \frac{\chi\text{-absorption of bleached oil} \times 100}{\chi}$$

Results and Discussions

All the samples were tested for their cation exchange capacity and swelling index. This was done with an object of finding out the variations in different deposits as regards the type and amount of clay. The results presented in Table 2 and 3 reveal that the type of clay is the same in all the deposits and the quantity varies slightly due to the presence of impurities. This is evident from the fact that cation exchange and swelling index values fall in a narrow range. The differences in the clay

TABLE 2. CATION EXCHANGE CAPACITY me/100g

Sample No.	Capacity	Sample No.	Capacity
S1	30.66	RA1	37.00
S2	29.00	RA2	16.60
S3	28.00	RA3	33.20
S4	30.66	RA4	24.00
S5	32.3	RA5	21.00
S6	34.00	RA6	26.00
S7	12.00	RA7	52.00
S8	32.3	RA8	22.08
S9	9.00	A-1 1	19.00
S10	31.6	A-1 2	19.00
S11	25.00	A-1 4	21.4
S12	28.00	A-1 5/1	26.3
S13	33.8	A-1 6	12.6
S14	31.6	A-1 7	15.38
S15	30.00	A-1 8	6.4
S16	34.00	1-2	10.00
S17	29.00	1-3	15.00
Daa1	27.6	1-4	14.4
Daa2	78.00	1-5	18.4
Daa3	88.00	1-6	20.00
Daa3/1	27.60	1-7	9.00
Daa3/2	23.00	1-8	8.50
Daa3/3	20.00	1-9	17.00
Daa4	25.00	1-10	29.00
Daa5	23.00	1-10/1	25.30
Daa8	28.66	1-10/2	18.00
Daa8/1	30.66	1-12	21.00
Daa8/2	25.3	1-13/1	26.30
1113/2	23.60	DBB6/2	37.3
I-14/1	26.40	DBB 6/3	30.3
I-14/2	27.60	DBB 7	30.3
I-14/3	5.00	DBB 9	32.00
I-15/1	17.00	DBB 10	30.3
I-15/2	27.00	K-1	36.60
I-16/1	26.40	K-2	31.00
I-17	14.30	K-3	23.00
I-18	13.00	K-4	23.00

(Contd. Table 2.)

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Sample No.	Capacity	Sample No.	Capacity
I-19	15.30	K-5	30.30
I-20	20.30	K-6	28.00
I-21	24.00	K-7	23.00
I-22	12.00	K-8	29.60
I-23/1	14.00	K-9	26.30
I-23/2	23.00	F-1	20.00
I-24	22.80	F-2	10.66
I-25	25.30	F-3	22.00
I-26	23.60	F-4	21.00
I-27	25.00	F-5	24.00
E-1	28.5	F-6	25.00
E-2	24.6	F-7	38.00
E-3	22.3	F-8	23.00
E-4	24.3	F-9	29.00
E-5	27.00	F-9/1	22.00
E-6	27.50	F-9/2	30.00
E-7	26.3	F-9/3	20.00
E-8	27.3	F-10	22.00
E-9/1	31.00	F-11	32.60
E-9/2	12.00	F-12/1	30.00
E-9/3	31.66	F-12/2	19.00
E-10	10.00	F-13	31.00
E-11	12.5	F-14	30.00
DBB 1	25.3	F-15	22.00
DBB 2	29.6	F-16	29.00
DBB 3	29.66	F-17	29.00
DBB 4/2	27.00	F-18	31.00
DBB 4/1	28.66	F-19	29.00
DBB 5	27.00	F-23/3	18.00

TABLE 3. SWELLING INDEX.

Sample	Swelling index	Sample	Swelling index
S4	3.20	K-1	3.08
S5	3.06	K-4	3.42
S10	3.10	K-7	2.80
S14	2.99	K-10	2.62
E1	2.92	RA-1	3.02
E7	2.96	RA-4	3.06
E9	3.45	RA-6	2.34
E11	2.67	Daa-3	3.21
I10	2.95	Daa-4	2.96
I18	3.34	A-2	2.98
I23	2.99	A-5	2.62
F-5	2.41	A-7	3.70
F9	2.80	A-8	2.94
F12	3.24	-	-
F23	3.04	-	-

content of various samples were minimised by water washing and rejecting the non-clay material which was not dispersible. The various analysis and characterisation tests were therefore, made on a few samples instead of all the samples.

Chemical analysis. Analysis of three samples has been presented in Table 4. These samples have been selected to represent the variations in chemical contents of almost all the samples.

Chemical analysis reveals little about the mineralogical composition of the clay because of isomorphous replacements

TABLE 4. CHEMICAL ANALYSIS.

	Sample No. A-I/1	Sample No. A-S/5	Sample No. FE-BN-2
Loss on Ignition	10.15	10.49	14.08
SiO ₂	54.96	56.10	56.64
Al ₂ O ₃	18.00	17.77	21.75
Fe ₂ O ₃	10.4	6.78	5.31
CaO	4.20	4.80	0.18
MgO	3.04	3.22	4.44
Na ₂ O	0.09	0.09	1.01
K ₂ O	0.21	0.21	0.52

and the possibility of the occurrence of more than one clay mineral in the same clay fraction. Analysis of montmorillonite mineral frequently show large values of H₂O high SiO₂ R₂O₃ ratios (4:1 or more) and low K₂O. About 20 percent Fe₂O₃ is indicative of pure nontronite and less than 1 percent MgO or 10% Fe₂O₃ is indicative of beidellite [9]. Illite or hydrous mica contain appreciable amounts of potash, approximately 6% as K₂O. In attapulgite-sepiolite minerals, magnesium is predominant. In attapulgite, Al₂O₃ and MgO are in equal proportion, whereas sepiolite is the magnesium end member and contains little alumina [1,10].

The chemical analysis indicates presence of montmorillonite group of minerals specially nontronite or beidellite because Fe₂O₃ is present upto 10 percent or more in some samples and K₂O content is low. Since MgO content is quite low, attapulgite and sepiolite are not indicated.

Different thermal analysis. Differential thermal analysis of fifteen samples was carried out. Their peak positions are given in Table 5. Endo-thermic peaks No.1,3 and 5 around 140°, 600° and 920° are shown by all the samples. Endothermic peak No. 2 around 425° is shown by all

TABLE 5. DIFFERENTIAL THERMAL ANALYSIS (HEATING RATE 10°C/MINUTE).

Sample No.	Peak positions		Degrees Centigrade		
	1	2	3	4	5
A-1/1	110(140)	-	550(600)		920
RA-1	110(140)	450	560(600)		920
RA-2	110(140)	-	560(600)		925
RA-3	110(140)	-	560(580)		920
R-4	110(140)	425	560(600)		920
R-5	110(140)	420	560(600)		920
R-6	110(140)	420	560(600)		920
R-7	110(140)	420	560(600)		920
R-8	110(140)	-	555(600)		920
A-2	140	425	600	800(+)	920
A-4	140	425	600	800(+)	920
A-6	140	425	590	800(+)	940
A-7	140	425	600	-	920
A-5/1	140	425	600	800(+)	920
A-8/5	140	-	600	800(+)	920

*(+) Indicates on exothermic peak.

the samples, except RA/1/1, RA-2, RA-3, RA-8 and A-8/5. Exothermic peak No. 4 at 800° is shown by A-2, A-4, A-6, A-5/1, A-8/5. Representative graphs of these samples are given in Fig. 1.

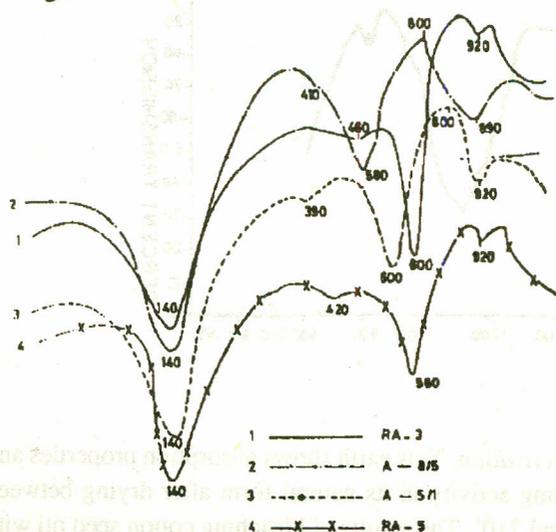


Fig 1. D.T.A. of Fullers earth from D.G. Khan.

The first endothermic peak in all the samples occurs around 140°. This peak can occur due to the presence of montmorillonite, nontronite and illite [11 a,b,c]. The second endothermic peak occurs around 425° and this is not given by any clay mineral expected to be present. This peak is due to the iron content [12,13] (Goethite) of the samples. Third endothermic peak occurs around 600°. This peak is observed in presence of illite and nontronite only. Montmorillonite does not show this peak. The corresponding peak shown by montmorillonite is at 700° which is missing in case of all these samples. There is an exothermic peak around 800° shown by some of the samples of A series. This peak is due to some phase transformation. The last endothermic peak around 920° is observed in case of illite and montmorillonite. One characteristic peak for beidellite which occurs around 560°-570° is missing.

Infra-red analysis. The infra-red absorption curves for the washed and the activated clay are presented in Fig 2 & 3.

In case of washed clay (Fig. 2) an absorption bend is shown between 2.8-3.2 microns and medium to weak absorption effect at about 6.2 micron and then a weak absorption shoulder at 8.55 micron and a comparatively strong shoulder at 8.95. A strong absorption effect is shown at 11.4 micron. Medium peaks are observed at 12.2 and 12.4 micron. The absorption effects at 2.78 to 3.2, 6.1-6.15; 8.95; 9.6 to 9.7; and 10.95 are shown by montmorillonite as well as illite [14]. The absorption effects at 6.2 and 8.55 are probably due to quartz and the effects at 12.2 and 12.4 are due to incomplete weathering of mica to illite.

The absorption curve for the activated clay (Fig. 3b) shows that absorption effect at 6.2 has weakened, the shoulder at 8.95 has taken the shape of strong peak and the strong peak at 9.6 has been converted to a shoulder. These changes indicate the corrosion of the lattice of the clay at some points while the overall structure remains intact.

X-Ray analysis. The X-ray diffraction data for the washed as well as activated clay is presented in Table 6.

TABLE 6. X-RAY POWDER DATA.

Radiation Cu K Exposure: 6 hrs Washed Clay			Camera: Debye Scherrer 114 mm dia Activated Clay		
dA°	I	Inf.	dA°	I	Inf.
4.47	40	IM	4.46	20	IM
4.23	40	OM	4.23	50	QM
3.33	100	I,Q	3.33	100	Q,I
2.57	10	IM	2.56	15	IM
2.429	3	Q	2.44	25	Q
1.81	5	Q	2.28	20	Q,I
1.535	5	Q	2.27	10	Q
1.37	5	Q	2.12	20	Q
-	-	-	1.97	10	Q
-	-	-	1.81	40	Q
-	-	-	1.66	20	Q
-	-	-	1.539	35	Q
-	-	-	1.499	2	I
-	-	-	1.369	50	Q

Intensities are determined visually.
Q = Quartz, I = Illite, IM = Illite-Montmorillonite.

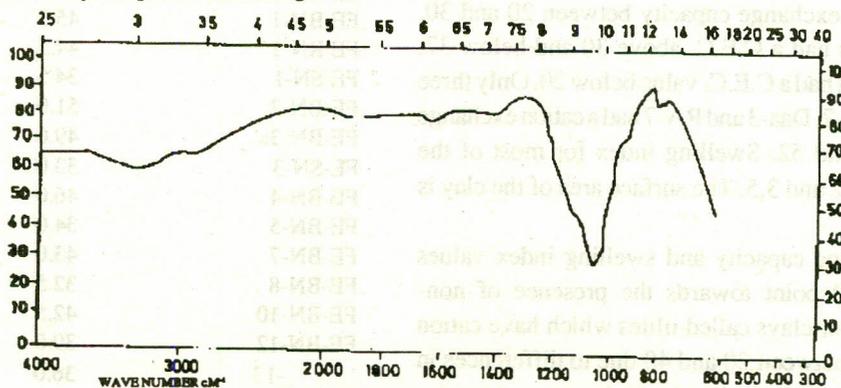


Fig 2. Wavelength in Microns.

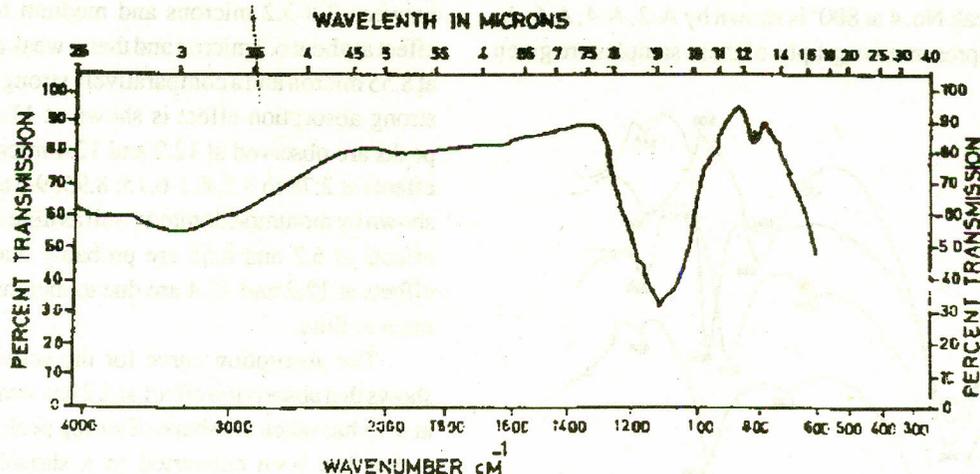


Fig 3.

Washed clay shows prominent diffraction lines at 3.33 \AA , 4.47 \AA , 4.23 \AA and 2.57 \AA in order of decreasing intensity. Pure illite shows the strongest line at 3.34 \AA . Illite and montmorillonite show intense and moderately intense lines at 4.45 \AA and 2.55 \AA . Calcium montmorillonite shows a moderately intense line at 4.4 \AA . Quartz also shows intense lines at 3.33 \AA and 4.23 \AA . Since DTA does not show the presence of quartz therefore, the amount of quartz present must be very small. The clay is, therefore, probably a mixed layer illite-montmorillonite clay. Diffraction lines in case of activated clay are the same but the diffraction line shown at 4.47 \AA has decreased in intensity and the diffraction lines at 4.23 \AA and 2.57 \AA have slightly improved in intensity. This is perhaps the effect of leaching out of various cations such as Fe^{+3} , Al^{+3} and Mg^{+2} etc.

Results of DTA, X-ray and Infra-red analyses indicate that the clay consists of nontronite, illite and montmorillonite and this is probably a mixed layer illite-montmorillonite clay in which there is appreciable substitution of iron in the direction of nontronite formation.

Cation exchange capacity and swelling. The results are presented in Table 2 and 3. Out of all the samples studied 65 samples had cation exchange capacity between 20 and 30. Thirty nine samples had a C.E.C. above 30 and below 37. Twenty five samples had a C.E.C. value below 20. Only three samples namely Daa-2, Daa-3 and RA-7 had a cation exchange capacity of 78, 88 and 52. Swelling index for most of the samples is between 2 and 3.5. The surface area of the clay is about 40000 sq. cm.

Cation exchange capacity and swelling index values between 20 and 40 point towards the presence of non-expanding three layer clays called illites which have cation exchange capacity between 20 and 40 due to differences in type and degree of isomorphous substitutions.

Activation. This earth shows adsorption properties and bleaching activity in its natural form after drying between 110° and 210° . The results of bleaching cotton seed oil with clay dried at 110° and 210° are presented in Table 7. Bleaching activity of various samples ranges from 33% to 50% decolourisation. Heating above 210° decreases the bleaching power of the clay. This clay is not expected to be activated by simple heating. The clays amenable to simple heating for activation are those containing attapulgite and sepiolite which contain water molecules in the structural channels running parallel to the amphibole chains [15]. These channels are large enough to admit molecules to occupy a considerable part of this space. Such clays, when heated between 300° - 500° loose the water contained in channels resulting in a great increase in the internal surface area [10] and can be activated in this manner [16]. Clays containing minerals of montmorillonite group are usually activated by acid treatment. Therefore, the best activation method was considered to be the acid-activation.

TABLE 7.

Sample No.	%Decolourization by clay heated at:	
	110°C	210°C
FE-BN-1	45.5	50.0
FE-RN-1	44.5	44.5
FE-SN-1	34.5	52.0
FE-BN-2	51.0	44.0
FE-BN-3a	49.0	53.5
FE-SN-3	33.0	47.5
FE-BN-4	46.0	41.5
FE-BN-5	34.0	37.0
FE-BN-7	43.0	44.0
FE-BN-8	32.5	45.5
FE-BN-10	42.5	49.0
FE-BN-12	39.0	61.5
-13	36.0	36.0

Acid activation. Activation by partial leaching with mineral acids appears to be a very simple process but in practice, it requires an extreme degree of control of process variable in order to obtain a product of requisite bleaching power. A wide variety of processes have been patented but very little information is available on the actual industrial process except those given in the classical article by Burghardt [17] and thereafter by Rich [18].

We have activated this Fuller's earth with HCl as well as H_2SO_4 . Activation depends on various factors such as strength of the acid, solid-liquid ratio, temperature of heating and proper washing of the clay after acid treatment. About 130 samples were activated with HCl and a few samples were activated with H_2SO_4 as well. A clay slurry containing 20% solids was activated refluxing with 4N HCl for 3 1/2 hrs. In case of sulphuric acid the same slurry was activated for 2 hrs. with 6 normal sulphuric acid. The heating was done with steam and the temperature of activation was approximately 100°. The results of bleaching activity of some selected samples are presented in Table 8. The bleaching activity of activated D.G. Khan earth has been compared with Terrana Optimum, the activated earth imported from W. Germany.

It is clear from the results presented in this table that both acids are capable of activating the earth to proper level to be useful industrially but H_2SO_4 proves a comparatively better activating agent. The details of activation studies shall be reported in a separate paper.

TABLE 8. BLEACHING ACTIVITY AFTER ACTIVATION WITH MINERAL ACIDS.

Sample No.	Bleaching of palm oil after activation with HCl		% bleaching of palm oil after activation with H_2SO_4	
	Red colour	Yellow colour	Red colour	Yellow colour
S-1	96.9	50.00	96.9	59.5
S-2	94.8	42.3	96.0	58.5
S-7	92.7	42.3	94.5	58.0
S-18	93.8	38.6	95.0	59.0
F-6	91.7	42.3	96.5	59.5
F-8	92.7	58.0	96.0	60.0
F-12/1	95.8	53.8	96.8	60.0
I-10	95.8	50.0	96.9	59.0
I-27	96.9	50.0	96.9	59.5
K-9	90.8	38.4	94.5	59.5
Daa-8/1	95.8	53.8	96.0	60.2
Daa-3/3	95.8	50.0	96.0	60.5

Bleaching by Terrana Optimum. % Red colour: 95.8 % Yellow colour 60.0

The activation studies were followed by evaluation of the activated clay samples by D.T.A. and it was found that there existed an optimum state of corrosion of the clay lattice by acid where the clay showed maximum bleaching activity. Figure 4 shows D.T.A. curves for a clay sample K-4,

activated under varying conditions. The activated sample presented by curve IV showed the maximum bleaching activity.

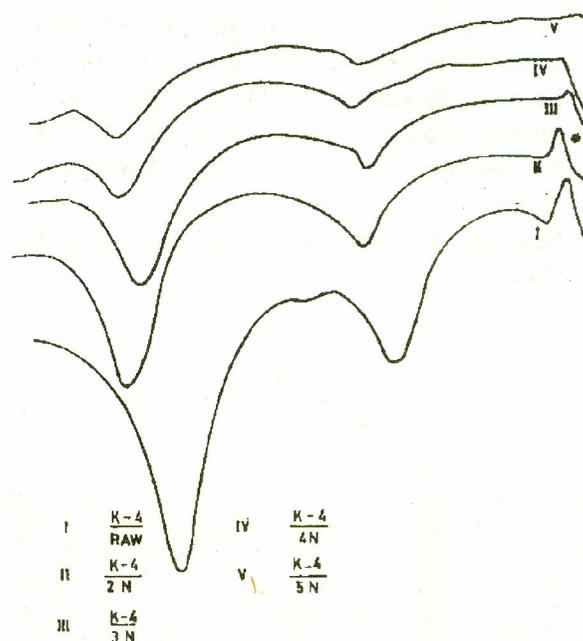


Fig 4. D.T.A. of Fullers earth Activated from D.G. Khan.

Conclusion

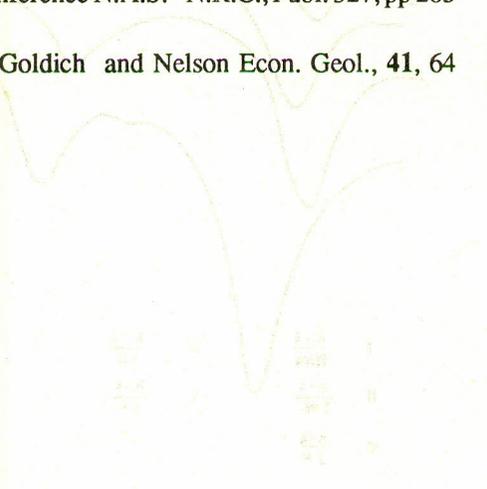
D.G.Khan Fuller's earth consists of minerals of montmorillonite group and comprises of nontronite illite and montmorillonite. This is probably a mixed layer illitemontmorillonite clay. This is not the type of clay which may be activated to a reasonable extent by simple heating. Acid activation process is more suitable for this and it has been found that by following proper activation procedure and selecting proper parameters it can be activated to such an extent that it can be used commercially.

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...activated with HCl and a few samples were activated with H₂SO₄ as well. A clay slurry containing 30% solids was activated refluxing with 4N HCl for 2 hours. In case of sulphuric acid the same slurry was activated for 2 hrs with a normal sulphuric acid. The heating was done with steam and the temperature of activation was approximately 100°. The results of bleaching activity of some selected samples are presented in Table 8. The bleaching activity of activated D.G. Khan clays has been compared with German samples, the activated clays imported from W. Germany.

...fraction from the amount present in the table that both acids are capable of reducing the cation to proper level to be used as a catalyst. However, H₂SO₄ gives a comparatively better activating agent. The details of activation studies will be reported in a separate paper.

Table 8. Bleaching activity of various clays with different acids.

Sample No.	Bleaching of pulp 50		Bleaching of pulp 50	
	with HCl	with H ₂ SO ₄	with HCl	with H ₂ SO ₄
1	92.9	92.9	92.9	92.9
2	94.8	94.8	94.8	94.8
3	92.7	92.7	92.7	92.7
4	92.8	92.8	92.8	92.8
5	92.1	92.1	92.1	92.1
6	92.8	92.8	92.8	92.8
7	92.8	92.8	92.8	92.8
8	92.8	92.8	92.8	92.8
9	92.8	92.8	92.8	92.8
10	92.8	92.8	92.8	92.8
11	92.8	92.8	92.8	92.8
12	92.8	92.8	92.8	92.8
13	92.8	92.8	92.8	92.8
14	92.8	92.8	92.8	92.8
15	92.8	92.8	92.8	92.8
16	92.8	92.8	92.8	92.8
17	92.8	92.8	92.8	92.8
18	92.8	92.8	92.8	92.8

...The activation studies were followed by treatment of the activated clay samples by D.T.A. which will show that there exists an optimum rate of conversion of the clay to be used as a catalyst. The details of the study will be reported in a separate paper.