

ACTIVATION OF D.G. KHAN FULLER'S EARTH WITH HYDROCHLORIC ACID

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Acid activation of washed D.G. Khan fuller's earth has been investigated with regard to parameters such as concentration of acid, percentage of slurry solids, duration of heating and temperature. It has been found that the fuller's earth may be activated to a maximum possible degree with varying sets of these parameters. The maximum activation achieved with (HCl) 6N acidulation for 2 hours activation time is suitable for producing a commercially acceptable product.

Key words: Activation, Clay, Hydrochloric acid.

Introduction

Fuller's earth/Bentonite deposits have been found at various places in Pakistan. Reasonably big deposits have been found at Dera Ghazi Khan and Attock (Punjab), Kirk (NWFP) and Thana Bulla Khan (Sind). There are several minor occurrences of bentonite in the whole of salt range in Punjab. Most of the deposits have been described as calcium bentonites (Zaki Ahmed 1969) while D.G. Khan fuller's earth is a mixed layer illite-montmorillonite clay (Yusuf *et al* 1989) According to surveys carried out by Punjab Mineral Development Corporation (Sulman *et al* 1969) (punjmin), the inferred reserves of fuller's earth of D.G. Khan are more than twenty five million tons. The fuller's earth found at various places is known to contain two groups of minerals, viz. smectites and attapulgites.

Fuller's earths belonging to smectite group are usually composed of montmorillonite, beidellite, nontronite, hectorite and saponite. Those belonging to attapulgite group contain polygorskite, sepiolite and attapulgite. Individual deposits usually contain any one of them as a predominant mineral. All the fuller's earths/bentonites known in Pakistan belong to smectite group (Ali and Shah 1962). Acid activation of fuller's earth is due to the corrosion of the lattice. There is an optimum extent of corrosion (Clarke 1985) for every clay. Since the corrosion of the lattice is known to depend upon concentration of acid, temperature of the reaction, solid liquid ratio of the slurry and duration of the reaction, it was decided to investigate all these factors in detail.

Experimental

Activation. The activation of the clay was carried out with hydrochloric acid under varying conditions specified in the

plan of activation presented in Table 1. Weighed/quantities of washed clay (Rafique and Yusuf 1996), water and acid were taken to meet the particulars of various sets of parameters according to the activation plan. The slurry from these components was refluxed in a round bottom flask fitted with a water condenser for a specified duration of time. At the termination of the experiment, the slurry was diluted with a large amount of water to stop the activation reaction. The activated clay was washed to the point where the pH of the slurry was around 4. The clay was filtered, dried at $100 \pm 5^\circ\text{C}$ and ground to pass through 100 mesh sieve.

Bleaching. Activated clay was used to bleach neutralised, moisture-free soybean oil. 0.25 g of clay was added to 25 g of oil in a 100 ml beaker, mixed thoroughly and heated in an oil bath at about 95°C with constant stirring for 30 min. The oil filtered quickly and the colour of the oil was measured on a Lovibond tintometer.

Bleaching power of activated clay is evaluated by noting the colour index of the bleached oil. Bleaching power, "per cent bleaching of activated clay", is calculated as follows:

Colour index of the oil = No. of red units x 10 + No. of yellow units

$$\% \text{ Bleaching} = \frac{\text{Colour index of the raw oil} - \text{Colour index of the bleaching oil} \times 100}{\text{Colour index of the raw oil}}$$

Results and Discussion

Acid activation is a process in which lattice of the predominant mineral is corroded to a certain extent. As a result active absorbent sites are created in the structure. It seeks to enhance properties already present in the mineral by manipu-

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Table 1
Plan of work

% Solid content of slurry	Normality of acid	Time in hours
16.7	2N	4,5,6,7,8,9,10,11,12,
	3N	2,3,4,5,6,7,8
	4N	2,2 1/2,3,3 1/2,4
	6N	1 1/2,2,2 1/2,3,3 1/2,4
	8N	1,1 1/2,2,2 1/2,3
20	2N	4,6,8,10,12,14,16,18
	3N	3,4,5,6,7,8,9,10
	4N	2,2 1/2,3,3 1/2,4,5,6,7
	6N	1,1 1/2,2,2 1/2,3,3 1/2,
	8N	4 1/2,1 1/2,2,2 1/2,3,3 1/2
28.57	2N	6,8,10,12,14,16,18,20
	3N	6,8,10,12,14,16,18
	4N	2,3,4,5,6
	6N	2,2 1/2,3,3 1/2,4,4 1/2
	8N	2,2 1/2,3,3 1/2,4

lating its chemical and physical attributes already present in the mineral without destroying mineral layer crystal structure. The optimum corrosion of the lattice is somewhere near half way of the octahedral or gibbsite layer. Cases of complete corrosion of gibbsite in various catalysts have been described (Takeshi 1968). In the present case, the clay under investigation has been proved to be a mixed layer clay in which the octahedral layer of the montmorillonite structure has undergone substitution by iron converting it to nontronite.

The corrosion of the lattice is brought about by heating the clay in suspension with strong mineral acid. The penetration of the acid to individual clay particles and the consequent reaction depends upon the concentration of the acid, temperature of the reaction, solid-liquid ratio of the slurry and duration of the reaction. Various combinations of these parameters were made to perform a number of activation and bleaching tests. Clay contents of the slurry were varied from 17 to 29% by weight, concentration of the acid from 2 to 8N and the duration of activation lasted from 1 to 20 h. The temperature during activation of suspension with hydrochloric acid remained at $100 \pm 5^\circ\text{C}$.

Table 2

% Solid content of slurry	Duration of reaction h	% Bleachability at acid normality				
		2N	3N	4N	6N	8N
16.7	1	-	-	-	-	77.01
	1 1/2	-	-	-	76.19	76.80
	2	-	75.80	75.00	76.40	75.05
	2 1/2	-	-	76.20	76.45	73.35
	3	-	76.00	76.60	76.25	71.80
	3 1/2	-	-	76.20	75.61	-
	4	75.81	76.18	75.20	74.32	-
	5	76.10	76.61	-	-	-
	6	76.20	77.90	-	-	-
	7	76.10	78.80	-	-	-
	8	76.12	78.20	-	-	-
	9	76.20	-	-	-	-
	10	76.20	-	-	-	-
	11	76.00	-	-	-	-
	12	75.80	-	-	-	-
	13	-	-	-	-	-
	14	-	-	-	-	-
	15	-	-	-	-	-
	16	-	-	-	-	-
17	-	-	-	-	-	
18	-	-	-	-	-	
19	-	-	-	-	-	

Table 3

% Solid content of slurry	Duration of reaction h	% Bleachability at acid normality				
		2N	3N	4N	6N	8N
20.00	1	-	-	-	74.40	76.78
	1 1/2	-	-	-	75.31	76.30
	2	-	-	73.38	75.80	75.38
	2 1/2	-	-	74.02	75.85	74.42
	3	-	73.61	74.66	75.05	74.35
	3 1/2	-	-	75.67	74.25	73.49
	4	58.10	73.80	76.80	73.40	-
	5	-	74.08	76.08	-	-
	6	58.21	75.00	74.84	-	-
	7	-	77.39	73.08	-	-
	8	58.48	79.05	-	-	-
	9	-	79.58	-	-	-
	10	58.80	78.19	-	-	-
	11	-	-	-	-	-
	12	60.01	-	-	-	-
	13	-	-	-	-	-
	14	66.06	-	-	-	-
	15	-	-	-	-	-
	16	66.68	-	-	-	-
	17	-	-	-	-	-
18	64.00	-	-	-	-	
19	-	-	-	-	-	
20	-	-	-	-	-	
Bleachability of standard clay		80.00	79.35	80.83	80.83	80.83

Table 4

% Solid content of slurry	Duration of reaction h.	% Bleachability at acid normality				
		2N	3N	4N	6N	8N
24.24	1	-	-	-	-	-
	1 1/2	-	-	-	75.10	76.63
	2	-	-	76.00	78.21	73.81
	2 1/2	-	-	-	75.82	73.42
	3	-	-	77.40	75.00	73.40
	3 1/2	-	-	-	75.00	73.41
	4	-	-	78.32	75.02	-
	5	-	-	-	75.00	-
	6	58.60	67.62	76.18	-	-
	7	-	-	73.33	-	-
	8	59.40	67.81	-	-	-
	9	-	-	-	-	-
	10	59.85	68.19	-	-	-
	11	-	-	-	-	-
	12	60.00	68.85	-	-	-
	13	-	-	-	-	-
	14	60.00	73.20	-	-	-
	15	-	-	-	-	-
	16	60.00	73.20	-	-	-
	17	-	-	-	-	-
18	60.21	-	-	-	-	
19	-	-	-	-	-	
20	60.20	-	-	-	-	
Bleachability of standard clay		80.00	79.35	80.83	80.00	79.80

Table 5

% Solid content of slurry	Duration of reaction h	% Bleachability at acid normality				
		2N	3N	4N	6N	8N
28.57	1	-	-	-	-	-
	1 1/2	-	-	-	-	-
	2	-	-	73.35	73.31	60.00
	2 1/2	-	-	-	74.94	58.00
	3	-	-	73.33	75.00	56.00
	3 1/2	-	-	-	73.30	54.63
	4	-	-	73.62	73.33	53.60
	5	-	-	-	73.30	-
	6	45.81	51.08	74.22	-	-
	7	-	-	74.87	-	-
	8	45.80	51.10	-	-	-
	9	-	-	-	-	-
	10	45.78	51.10	-	-	-
	11	-	-	-	-	-
	12	45.82	51.22	-	-	-
	13	-	-	-	-	-
	14	46.02	51.60	-	-	-
	15	-	-	-	-	-
	16	45.97	53.20	-	-	-
	17	-	-	-	-	-
18	46.12	55.51	-	-	-	
19	-	-	-	-	-	
20	46.02	-	-	-	-	
Bleachability of standard clay		79.35	80.83	80.00	80.00	80.00

The results of bleaching power during this investigation represented in Tables 2, 3, 4 and 5 reveal that the maximum bleachabilities, 78.80, 79.58, 78.32 and 78.21% are achieved at acid strength 2N, 3N, 4N and 6N, with the time of reaction, 7, 9, 4 and 2 h and slurry composition, 16.7, 20.0, 24.24, 28.57% respectively. The results are close enough to the imported clay, terrana optimum, the largest tonnage of which is consumed at present by the local oil industry. The results reveal that the maximum increase in the surface area beyond which bleaching performance falls progressively occurs at acid severity 4N and 6N with activation time 4. and 2 h respectively and 24.24 % solid contents. In view of high energy cost and low cost of acid (HCl), 6N acidulation for 2 h activation time is preferable.

Particle size (Clarke 1996) of activated clays also plays an important role. The finer clays below 120 mesh provide better bleaching and decolourising properties owing to the availability of greater surface area. The action of the clay is to absorb coloured matter and impurities on the surface of individual particles. But because of inefficient filtration and

greater amount of oil retention on the filter cake, the particle size below-120 mesh is not suggested.

References

- Ali S T, Shah I 1962 *The bentonite resources of Pakistan, Symposium on industrial rocks and minerals*, pp 153-160.
- Clarke G M 1985 Special clays review, industrial mineral. **22-52** (216).
- Rafique M, Yusuf M 1996 Activation of fuller's earth of D.G. Khan with sulphuric acid. *Pak J Sci Ind Res* **39** 9-12.
- Sulman, Khalid M, Ali S T, Ahmed W 1969 *A report on exploration and evaluation of lime-stone, gypsum fuller's earth deposits in D. G. Khan District by Punjmim*.
- Takeshi H 1968 Montmorillonite deposits in Japan Nendo Kagaku **8** (3-4) pp 10-18 in Japanese.
- Yusuf M A, Iqbal M Mian, Rafiq M, Ayub M 1989 Characterisation of fuller's earth of D. G. Khan. *Pak J Sci Ind Res* **32** (12) 789-804.
- Zaki Ahmed 1969 Records of geological survey of Pakistan. **15** Part-3 65-69.