

MINERALOGY OF SWAT KAOLINITE

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Fifty one samples of the raw and the beneficiated Swat Kaolinite have been analysed. Two representative samples of the raw and the washed kaolinite have been prepared from 79 samples received and their DTA and X-ray studies made. On the basis of the data obtained, the mineralogy of the deposit and that of the treated kaolinite has been ascertained. X-ray studies indicate that the mineral kaolinite in the raw samples is between 15 to 20%, whereas in the washed samples it is between 45 to 50%.

Introduction

Clays, in general, are the result of the natural decomposition over the course of many centuries of the mineral feldspar, one of the main constituents of granite, the other constituents are quartz, mica and tourmaline. The process by which feldspar was changed naturally into clay is known as "kaolinization", the resulting product being known as China clay in U.K. but as kaolin outside of Britain. All incomplete weathered feldspathic deposits have, as their constituents, feldspars which are anhydrous aluminium silicates of potassium, sodium or calcium, in which one base generally predominates.

The Swat kaolinite deposits, located in Swat State about 14 miles north west of Mingora are linked by an all weather non-metalled road. The main clay deposit extends between the villages of Taghna on the eastern side and Shah Dheri on the western side which are a little over two miles apart from each other. The whole deposit combined in Fig. 1 A and B may be divided into three main parts, the western part, the middle part and the eastern part.¹ The eastern and the middle parts are about half a mile long with an average width of 800' and 600' respectively. The western part is more than half a mile long and variably 100 to 1000' wide. Exploratory pits having a minimum of 5' to a maximum of 30' depth have been dug out but none of them reached the depth limit of the deposits. It may, therefore, be concluded that the reserved estimate of the deposit is quite economical and its commercial exploitation may be taken up. According to an earlier report,² the total kaolin is about 258,700 tons as the kaolin recovered is 40-50% pure, only 120,000 tons of kaolin remain to be used. Unless a thorough survey is carried out it is premature to calculate the amount of the deposit.

The Swat clay, in fact, is a product of the partial decomposition of feldspathic bands which occur with the parent rock. The samples show that most of the feldspathic rocks have not been fully decomposed to kaolin and, therefore, quite large sizes of unweathered pieces of feldspar are found in the clay. Some properties of this clay have been reported previously^{3,4} but no attempt has been made to investigate the mineralogical composition of the material. Although there are many potential ceramic and other uses for kaolinic materials of the type occurring in Swat State, this investigation has been limited to a study of their mineralogical nature which will ultimately help in finding out its properties and uses.

79 samples received from the Geological Survey, which have been collected from the selected exploratory pits (as shown in Figs. 1A and B) of the eastern and middle parts of the main deposit, bear the symbol MF, while those with AT symbol are from the western part of the deposit. A few samples have also been collected from the minor deposits, trenches and tunnels. All the samples, as stated earlier, have been taken from a depth varying from 5 to 30'.

Experimental

Out of the 79 samples received, only 51 have been selected for chemical analysis. 28 samples have been left over because of their close proximity with those selected for analysis. But the raw and the washed representative samples have been carefully prepared from the total 79 samples. The chemical analyses have been carried out according to the improved standard silicate analysis method.⁵ Alkalis have been determined using a flame photometer of EEL type. The chemical analysis of 51 raw and the washed samples have been presented in Table 1.

TABLE I.—CHEMICAL ANALYSIS OF RAW AND WASHED KAOLINITE SAMPLES.

No.	Sample No.	Pit. No.	Sample condition	L/I %	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	Na ₂ O %	K ₂ O %	Total %
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	65MF1	10	Raw	4.13	48.95	32.03	1.60	8.36	1.29	2.59	Traces	99.96
			Washed	7.55	49.33	34.23	.68	4.57	1.23	2.46	Traces	100.05
2.	65MF5	22	Raw	3.64	48.44	31.5	1.5	9.67	1.43	3.09	0.69	99.96
			Washed	9.55	50.44	32.18	0.40	4.83	0.58	1.65	0.38	99.99
3.	65MF7	23	Raw	4.56	45.45	33.25	2.30	9.25	2.85	2.04	0.20	99.90
			Washed	8.80	48.55	35.68	0.57	3.22	1.36	1.74	0.17	100.09
4.	65MF8	15	Washed	11.67	46.48	33.89	1.76	1.61	2.85	1.75	0.15	100.06
5.	65MF10	20	Raw	4.45	47.68	32.72	1.78	10.68	1.70	1.81	0.19	100.01
			Washed	8.60	47.88	34.65	0.85	5.34	1.52	1.11	0.09	100.04
6.	65MF12	30	Raw	5.27	46.30	32.86	3.15	8.05	2.75	1.39	0.20	99.97
			Washed	9.34	47.80	34.83	.97	3.75	2.01	1.05	0.16	99.99
7.	65MF13	17	Raw	5.14	44.61	34.60	2.65	8.90	2.01	1.95	0.14	100.00
			Washed	11.47	47.28	35.05	0.45	2.63	1.04	1.05	0.07	100.04
8.	65MF14	46	Raw	4.74	47.75	34.07	1.33	10.93	0.52	1.45	0.15	99.94
			Washed	13.23	47.70	34.27	0.41	2.79	0.67	0.80	0.09	99.96
9.	65MF15	35	Raw	5.45	45.68	31.01	6.00	9.08	1.64	1.0	.10	99.98
			Washed	7.60	47.32	33.6	1.14	8.12	1.25	.8	.09	99.93
10.	65MF17	8	Raw	5.10	45.86	32.00	3.00	10.19	1.11	2.04	0.59	99.89
			Washed	10.18	47.95	34.67	0.43	3.47	1.50	1.50	0.28	99.98
11.	65MF18	32	Raw	5.13	47.00	31.94	1.56	10.94	1.44	2.78	0.20	99.99
			Washed	9.60	48.66	35.00	0.50	3.05	1.48	1.74	0.12	100.03
12.	65MF19	47	Raw	4.01	45.26	36.10	1.65	9.91	1.74	1.20	0.10	99.97
			Washed	7.60	46.75	36.40	0.68	5.48	1.80	1.19	0.09	99.99
13.	65MF20	33	Raw	4.42	45.02	30.91	3.34	12.07	2.62	1.22	0.30	99.90
			Washed	7.24	48.97	35.91	0.87	3.75	1.89	1.09	0.21	99.93
14.	65MF22	52	Raw	4.02	42.33	30.40	6.25	12.12	3.60	1.01	0.10	99.83
			Washed	8.00	46.30	36.10	1.10	6.22	1.22	.80	.09	99.83
15.	65MF23	54	Raw	4.80	46.15	31.50	5.00	9.15	2.00	1.12	.08	99.98
			Washed	8.50	47.75	36.50	0.60	4.06	1.98	.59	.05	100.03
16.	65MF25	1	Raw	4.58	43.65	33.24	2.76	10.46	2.69	2.23	0.20	99.91
			Washed	11.87	44.63	35.59	0.42	4.32	1.65	1.31	0.13	99.92
17.	65MF28	Main tunnel	Raw	4.15	43.34	33.50	3.05	11.27	1.95	2.28	0.45	99.99
			Washed	9.67	46.05	36.31	0.92	3.24	1.85	1.60	0.38	100.02
18.	65MF30	Trench No. 1	Raw	5.53	44.96	28.63	6.37	10.93	2.36	1.10	0.11	99.99
			Washed	8.82	47.85	34.35	2.50	3.56	1.85	.9	.10	99.93
19.	65MF32	Trench No. 2	Raw	5.86	45.56	32.94	2.91	8.44	1.75	2.22	.18	99.96
			Washed	11.75	46.12	34.98	1.23	3.21	1.03	1.6	.12	100.04
20.	65MF34	10	Raw	5.50	43.80	31.43	3.58	11.40	2.33	1.55	.29	99.88
			Washed	12.00	46.99	35.19	0.96	2.69	0.83	1.15	.16	99.97
21.	65MF35	13	Raw	4.23	43.48	31.89	4.11	12.40	2.41	1.22	.18	99.92
			Washed	12.57	45.65	34.30	0.95	4.38	0.93	1.16	.16	99.97
22.	65AT10	50	Raw	4.40	45.23	30.65	4.40	10.70	3.10	1.12	0.30	99.90
			Washed	9.00	47.65	34.54	0.77	4.33	2.41	0.95	0.25	99.92

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(Table 1 Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
23.	65AT12/2	.. Trench No. 2	Raw .. Washed ..	5.65 9.18	44.00 46.05	33.33 34.33	1.25 0.80	12.65 7.63	1.25 1.30	1.55 .62	.25 .09	99.93 100.00
24.	65AT14	.. 56	Raw .. Washed ..	5.00 11.40	43.97 47.88	29.58 34.59	4.45 0.41	12.80 1.90	2.19 2.35	1.56 1.15	0.35 0.30	99.90 99.98
25.	65AT 15	.. 58	Raw .. Washed ..	5.60 9.05	46.15 48.12	34.62 35.25	1.23 0.50	9.36 4.36	1.06 1.15	1.70 1.37	0.25 0.21	99.97 100.01
26.	65AT 16	.. 59	Raw .. Washed ..	5.70 9.80	43.65 47.66	32.72 36.30	3.53 0.45	10.90 2.98	1.66 1.08	1.50 1.45	0.25 0.20	99.91 99.92
27.	65AT 18	.. 66	Raw .. Washed ..	4.66 9.05	45.95 48.45	34.63 34.76	2.2 0.82	10.00 4.06	1.19 0.93	1.29 0.93	Traces Traces	99.95 100.00
28.	65AT 19	.. 31	Raw .. Washed ..	5.85 9.09	46.25 48.37	32.20 35.13	2.51 0.37	10.01 4.09	1.09 1.41	1.64 1.32	0.32 0.28	99.87 99.97
29.	65AT 20	.. 26	Raw .. Washed ..	8.61 15.45	39.42 40.02	28.35 29.67	3.65 0.42	16.75 11.80	1.08 0.50	1.70 1.11	0.30 0.20	99.86 99.98
30.	65AT 21	.. 5	Raw .. Washed ..	4.60 8.85	46.8 50.50	33.80 33.47	2.50 0.63	9.41 4.57	1.66 0.75	1.02 1.00	0.13 0.10	99.92 99.87
31.	65AT 22	.. 10	Raw .. Washed ..	9.00 10.30	43.70 46.21	30.96 34.47	1.12 0.33	12.4 7.12	1.81 1.20	1.10 0.48	Traces Traces	100.09 100.10
32.	65AT 23	.. 22	Raw .. Washed ..	7.50 12.80	43.80 45.05	32.50 36.81	5.00 1.10	8.90 3.05	1.80 0.83	0.50 0.40	Traces Traces	100.00 100.04
33.	65AT 24	.. 19	Raw .. Washed ..	4.75 12.12	41.35 42.00	32.00 31.80	3.60 1.00	13.9 9.65	2.84 2.60	1.26 0.90	0.24 0.10	99.94 100.17
34.	65AT 25	.. 20	Raw .. Washed ..	7.44 12.65	41.80 45.85	31.45 34.12	4.70 1.01	10.40 4.06	1.69 1.16	2.25 1.15	0.27 0.15	100.00 100.15
35.	65AT 25/(2)	.. 4	Raw .. Washed ..	8.40 12.50	43.10 45.40	34.55 35.24	2.45 0.42	9.91 5.60	1.08 0.50	0.30 0.25	0.15 0.08	99.94 99.99
36.	65AT 27/(2)	.. 6	Washed ..	13.21	46.00	33.93	0.12	3.09	1.94	1.55	0.25	100.08
37.	65AT 28	.. 2	Raw .. Washed ..	8.75 10.82	43.30 45.85	34.25 35.95	1.35 0.71	9.41 5.34	1.95 1.02	0.90 0.41	Traces Traces	99.91 100.10
38.	65AT 29	.. 37	Raw .. Washed ..	9.00 13.10	46.05 46.22	33.26 34.32	2.65 0.68	6.86 3.05	0.92 1.16	1.15 0.60	0.05 0.02	99.94 100.15
39.	65AT 30/2	.. Tunnel	Raw .. Washed ..	9.85 12.40	43.75 46.80	32.55 35.13	1.95 0.35	9.41 3.8	1.95 1.2	0.54 0.50	Traces Traces	100.00 100.18
40.	65AT 30/5	.. Tunnel	Raw .. Washed ..	5.65 12.16	45.65 46.89	33.55 34.54	2.70 0.62	10.02 3.56	0.88 1.20	1.5 1.10	Traces Traces	99.95 100.07
41.	65AT 31	.. North drift	Washed ..	10.13	46.54	36.12	0.93	2.54	1.18	2.10	0.40	99.94
42.	65AT 32	.. South drift	Washed ..	11.43	47.61	35.38	0.12	2.14	1.89	1.31	0.29	100.17
43.	65AT 33	.. 14	Raw .. Washed ..	5.90 11.65	45.70 46.85	31.23 32.78	2.35 1.00	11.85 6.04	1.50 0.85	1.36 0.90	0.09 0.03	99.98 100.1
44.	65AT 34	.. 38	Raw .. Washed ..	5.85 12.40	45.25 47.09	31.85 32.33	3.50 1.67	8.94 2.73	1.85 1.81	2.16 1.63	0.45 0.32	99.85 99.98
45.	65AT 35/1	.. 1	Raw .. Washed ..	8.90 10.00	43.30 47.00	36.85 35.31	0.65 0.60	6.61 5.34	2.28 1.19	1.26 0.60	0.14 0.06	99.99 100.10
46.	65AT 36	.. 12	Raw .. Washed ..	3.25 11.23	44.35 46.55	34.64 36.00	1.52 0.50	12.75 2.46	1.57 1.50	1.70 1.60	0.09 0.06	99.87 99.90

(Table 1 Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	
47.	65AT 37/2	..	7	Raw ..	5.55	45.95	34.60	1.40	9.19	0.66	2.19	0.36	99.85
				Washed ..	9.30	47.25	36.81	0.27	3.79	0.78	1.53	0.27	99.90
48.	65AT 38	..	9	Raw ..	5.85	43.85	32.75	2.75	10.63	1.68	2.10	0.30	99.91
				Washed ..	10.55	46.82	36.03	0.52	2.63	1.43	1.76	0.24	99.98
49.	65AT 39	..	8	Raw ..	4.67	45.07	34.15	1.85	11.36	1.08	1.55	1.25	99.98
				Washed ..	9.50	48.62	36.66	0.22	2.01	1.45	1.33	0.20	99.99
50.	65AT 40	..	39	Raw ..	3.70	41.30	35.25	4.20	12.75	1.73	0.86	0.20	99.99
				Washed ..	8.45	47.95	35.31	1.02	4.50	2.10	0.63	0.13	100.09
51.	65AT 41/2	..	Trench No. 1	Raw ..	5.65	46.00	32.16	2.34	10.73	1.33	1.48	0.24	99.93
				Washed ..	12.95	46.25	33.59	0.66	3.17	1.85	1.35	0.18	100.00

against a stream of water in a 120 mesh sieve and later on passed through a 200 mesh sieve. The clay suspended water, after passing through the sieves (120 mesh) was made to settle. Most of the clear water was then drawn off and the milky mass of clay was obtained. The percentage of clay obtained from MF samples varies between 6 and 41% with an average of 15.65% whereas in AT samples, the quantity of clay obtained is between 8 and 51% with an average of 25.97%.

Thus the average washed clay, obtained from the 79 samples, is 21.34%. This average comes to about 17% if the samples are washed through a 200 mesh sieve. From the cornish china clay mines, only 13% of china clay is extracted⁶ in which the mineral kaolinite is about 80-85%, the rest being soda and potash spars, whereas in the washed samples under study the mineral kaolinite is 50-60%. It is hoped that with the improved techniques of washing, the percentage of pure kaolin may be increased.

The chemical analyses, mineralogical composition, DTA and X-ray properties of the raw and the washed representative samples of kaolinite have been determined. Some details of the DTA and X-ray techniques have already been reported in earlier papers.^{7,8} The Norelco diffractometer has been used and '2 θ ' values obtained have been converted to 'd' values. The derived 'd' values have then been compared with the standard values of the minerals given in the A.S.T.M. An approximate percentage of the minerals, by comparing the intensities of the 'd' values, has been determined.

CHEMICAL AND MINERALOGICAL COMPOSITION

From the chemical analyses of 51 samples of the Swat kaolinite, as given in Table 1, it may be seen

that the raw and the washed kaolinites are essentially an admixture of albite, anorthite, bytownite labrodarite and kaolinite. Some of the minor constituents such as biotite, muscovite, hornblende, tourmaline, apatite and complex magnesium silicates are also present, though some of them are present in traces. The chemical analyses, given in Table 1, show the quantities of oxide elements present in the samples but in order to have an idea of their mineralogical nature, it is necessary to calculate the rational composition by its ultimate analysis. This process of calculation is of a complex nature. The rational analysis, is, in fact, useful only in case of mixtures of a better grade of clay in which the variations of the ingredients can only be within the comparatively narrow limits. Although the rational or mineralogical analysis may be an invaluable aid to the investigator of high grade clays, yet the methods are far from satisfactory.

Following the technique of Koenig,⁹ the mineralogical compositions of the raw and the washed representative samples have been calculated and presented in Table 2. It may be seen that feldspars form the major portion of the raw kaolinite varying between 60-65% of the total including about 13% albite and 50% anorthite. Mineral kaolinite coming next varies between 15-25% according to the methods used. As shown in Table 2, if magnesium oxide is neglected the percentage of clay comes to about 26.8% but if it is calculated as some kind of magnesium silicate, the clay reduces to 17% giving about 10% of complex magnesium silicates which include biotite and hornblende, the latter mineral is an aluminosilicate of calcium, magnesium and iron found in impure clays and feldspathic materials, and in those particles of the clay which have been derived from dark coloured igneous rocks. These dark pieces sorted out from the samples have been

TABLE 2.—APPROXIMATE MINERALOGICAL COMPOSITIONS OF THE REPRESENTATIVE RAW AND WASHED KAOLINITE MATERIALS.

Minerals	Raw kaolinite		Washed kaolinite	
	No. 1	No. 2	No. 1	No. 2
Na. spar (Albite)	13.12	13.12	10.48	10.48
Ca spar (Anorthite)	50.87	50.87	23.63	23.64
Mica	1.35	1.35	.48	.48
Magnesium silicates	11.80	—	9.05	—
Kaolinite	17.0	26.8	51.57	59.57
Quartz	—	.84	—	—

analysed, and the results confirm that samples contain minerals like biotite and hornblend. Micas and apatite are found in minor amounts. The presence of apatite may be confirmed by the amount of P_2O_5 obtained in the chemical analyses of the raw and the washed representative samples (Table 3).

The mineralogical composition of the washed sample shows that in this clay the major constituents are kaolinite and feldspars (albite and anorthite) with about 10% of soda-spar, 23% lime-spar and 50-60% of kaolin. Raw kaolin is a mixture of true clay, undercomposed feldspars and free quartz. Many of the impurities, found in the original rock such as mica, titanium and iron compounds and some other constituents in small quantities, still remained in the raw kaolinite and continued to be present in the washed samples. The mineralogical results, obtained from the raw and the washed samples, when compared, show that after washing there is an appreciable reduction (Table 2) in anorthite but not much in albite. This point will be explained while discussing the X-ray results.

CHEMICAL COMPOSITION AND FUSIBILITY

Kaolin generally contains less than 2% alkalis and smaller quantities of iron, lime, MgO and

TiO_2 . Because of its purity, kaolin has a high fusion point which ranges between 1750-1770°C.⁶ A slight addition of fusible impurities lowers its refractoriness. The softening points of the raw and the washed samples have been determined and found to be 1380°C and 1600°C respectively. The washed mixture after passing through a 120 mesh sieve, deforms at 1600°C whereas the same mixture, when passed through a 200 mesh sieve, deforms at a slightly higher temperature at 1615°C. Sample No. 39 though passed through 120 mesh sieve, deforms at 1620°C. The chemical analyses of all the three samples, given in Table 1 and 2 clearly explain the reason. It may be seen that the -120 mesh mixture after passing through a 200 mesh sieve loses some of its low fusion feldspars and thus its deformation temperature increases by 15°C. Similarly sample No. 39 without passing through a 200 mesh sieve, has a higher softening point because its composition contains less fluxing materials than that of a -200 mesh clay. The representative raw mixture softens at 1380°C because it contains more than 60% feldspars (softening points varying from 1200°C to 1550°C) with many other low melting substances as shown in Tables 2 and 3. Other raw samples deformed at temperatures ranging from 1300 to 1450°C. In the washed samples the amount of kaolinite ranges between 50-60% the remaining being albite and anorthite having 1200° and 1550°C softening points respectively. These feldspars exert their influence in lowering the deformation temperature of the clay by 100-150°C. In considering the changes which occur in the fusion of the clay, it has to be noted that clay is not a substance of definite composition but consists of a mixture of minerals each having its own range of fusion. In general, the temperature of fusion of a clay will come down with an increase in the percentage of total fluxes and the different fluxes exert a different fluxing influence. During the heating of a clay a reaction occurs between the silica, alumina and the various fluxes giving rise to the formation of complex silicates. The esti-

TABLE 3.—CHEMICAL ANALYSIS OF THE REPRESENTATIVE AND SORTED (BLACK AND WHITE) KAOLINITE SAMPLES.

	L/I	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	
Representative raw sample	..	5.35	45.03	32.16	.187	3.15	10.30	1.90	1.65	.18	.09	99.99
Representative washed (-120 mesh)		10.36	47.15	33.85	.09	.80	4.96	1.26	1.30	.12	.04	99.93
Fraction (-120 × 200) mesh	..	7.34	46.80	33.25	—	1.00	7.79	2.00	1.55	.14	—	99.87
Representative washed (-200 mesh)		10.63	48.50	33.30	—	.65	3.24	1.25	1.25	.10	—	99.82
Black portion	..	4.70	41.91	17.03	—	17.5	12.00	4.06	—	—	—	97.20
White portion	..	7.59	47.25	32.13	—	1.13	8.15	2.4	—	—	—	98.65

mation of the refractoriness, therefore, by means of the percentages of alumina and fluxes alone, leads to erroneous results.

DTA AND X-RAY STUDIES

Some information of the percentage of all rocks forming minerals present in the kaolinite is essential in studies covering the properties and uses of kaolinite. Having this in view a detailed investigation has been conducted involving a study of the thermal and X-ray properties of the mineral.

In general, the thermal reactions of the kaolin minerals may well be related to their structural concepts. The first attempt in this connection has been made by Insley and Eweli¹⁰ who characterised the thermal curves of the kaolin family and related these curves to the structure of kaolinite. The curves of the raw and the washed samples obtained along with a standard English China clay are presented in Fig. 3. By heating kaolin the first real reaction occurs between 500-600°C when the chemically bound water is liberated and an exothermic reaction is produced. The metakolin phase is then found in the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ which is called an amorphous substance, an oxide mixture or semi crystalline material. Further heating will result in a strongly exothermic reaction between 900-1000°C. Various suggestions on the interpretation of this reaction between 900-1000°C have been made. In 1959, however, Briendly and Nakahira established that

some kind of spinal phase has been formed with the composition of $\text{Si}_3\text{Al}_4\text{O}_{12}$ which, later on, at 1100°C changes to mullite. Thus the formation of the silicon spinel at 925°C gives the strong exothermic peak.

The raw and the washed representative samples of kaolinite as shown in Figs. 2A and B give broad peak at about 110°C. The only peak given by the kaolin group below 500°C is the adsorbed water peak at about 150°C and due to the associated impurities the thermal curves may give a peak anywhere between 100-200°C. It is thus known that both the samples contain some adsorbed water which are mainly due to the fact that they are poorly crystallized. If the crystal imperfection is significant enough as is the case with regard to the samples under discussion, there should be a detectable amount of water as shown by the slight endothermic peaks in the range of 100-150°C. The major endothermic peak may be seen occurring between 500°C to 650°C with a maximum at 575°C and 560°C as compared to 575°C in the case of the English kaolin (Fig. 2C). This, as it has already been discussed, is the result of the breakdown of the structure of kaolinite brought about by the removal of the chemically held water in the clay lattice. Now, coming to the last exothermic peak which is really a characteristic of a well crystallized kaolinite, it may be seen from the thermal curves that the raw kaolinite does not give at all any indication of an exothermic peak; instead it gives an endopeak at 960°C. This clearly indicates that the small

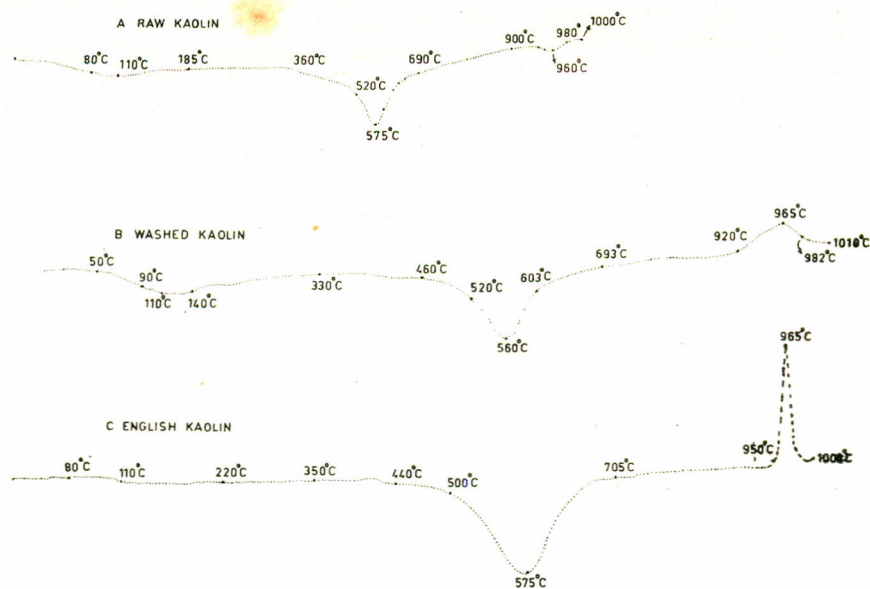


Fig. 2.—DTA curves of raw, washed Swat kaolinite along with English kaolinite.

quantity of kaolinite present in the sample (10-20%) has not been able to give an exopeak and has been suppressed by the feldspars present in large quantities. The sharpness of the exothermic peak is generally related to the degree of crystallinity whereas the poorly crystallized kaolinite gives a more rounded peak. This has been observed in the case of the washed sample which gives a subdued and broad exothermic peak at 965°C. In fact, interlayered (material mixtures) and poorly crystallized kaolinites do not show the exothermic peak, probably due to the broad temperature-range of the recrystallization. It is only poorly crystalline samples that present ambiguous problems in interpretation. In general, the depression of the peak is characteristic of the poorly crystallized kaolinite and this has been reflected in the broad endopeak and in the subdued exopeak of the washed kaolinite. Subdued reaction is also due to the impurities (feldspar etc.) present in the sample. From the above discussion it may be concluded that the pure kaolinite in the washed sample is not more than 50 or 60%.

The X-ray diffraction patterns of the raw and the washed kaolinite have been presented in Figs. 3A and B and the obtained 'd' values with their intensities are given in Table 4. These 'd' values and their intensities roughly give the quantities of the actual minerals present in both the samples. The raw sample indicates that its major constituents are bytownite and labradorite with small amounts

of kaolinite, albite, anorthite quartz and micas. All these minerals are present in the order cited. As the deposits are basic in nature as also confirmed by microscopic studies, the presence of appreciable amounts of free albite, anorthite and oligoclase has been ruled out.

According to a rough estimation, the total amount of plagioclase feldspars, such as bytownite and labradorite is about 60-70%, kaolin 15-20% quartz 5-10% and micas about 5%. The quartz, as indicated by the X-ray pattern, may have been liberated during the decomposition of some of the silicates, such as spars. The X-ray pattern of the washed kaolinite shows that the kaolinite is not more than 50% of the total usually 45-50%. The other constituents are bytownite and labradorite and a mixture of the two in various proportions along with some magnesium silicates.

It is known that albite and anorthite form extensive series of solid solutions. Two forms of such solid solutions are expected to be present in both the samples of kaolinite, and they are bytownite and labradorite having very similar 'd' values. It may also be seen that in the raw kaolinite the amount of bytownite is greater than labradorite, whereas after washing, it has been reduced. The only explanation which could be put at this stage is that during washing the coarse particles of bytownite have been removed more easily than that of the labradorite. The hardness of labradorite is 5-6,¹² whereas the hardness of

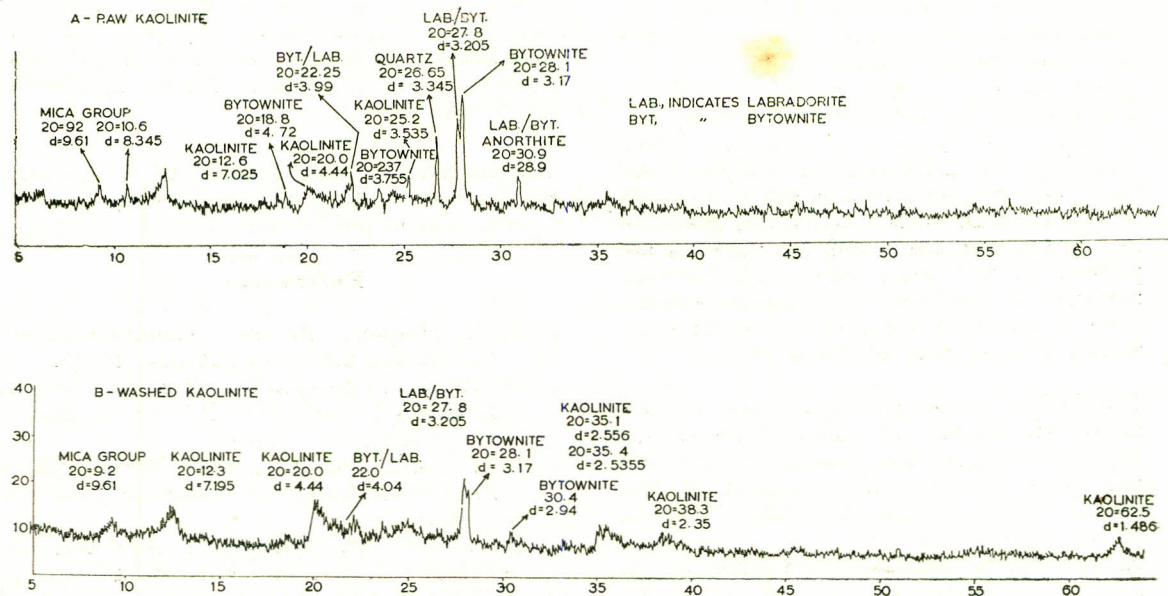


Fig. 3.—Diffraction patterns of Swat kaolinite: A (raw) and B (washed).

TABLE 4.—('d') VALUES OF THE MINERALS DETECTED IN RAW AND WASHED SWAT KAOLINITE ALONGWITH THEIR INTENSITIES.

Mica Group				Kaolinite				Plagioclase Series				Quartz			
Raw	I	Washed	I	Raw	I	Washed	I	Raw	I	Washed	I	Raw	I	Washed	I
9.61	15	9.61	25	7.025	35	7.195	45	4.72 (B)	12	4.04 (A,B,L)	40	3.345	50	—	—
8.345	15	—	—	4.435	20	4.440	65	3.99 (A,B,L)	30	3.205 (B,L)	100	—	—	—	—
—	—	—	—	3.535	25	2.556	40	3.755 (B)	15	3.17(B)	85	—	—	—	—
—	—	—	—	—	—	2.535	40	3.205(B,L)	80	2.94 (B)	25	—	—	—	—
—	—	—	—	—	—	2.35	30	3.17 (B)	100	—	—	—	—	—	—
—	—	—	—	—	—	1.486	33	2.89(A,B,L)	25	—	—	—	—	—	—

I. Indicates intensity of X-Ray reflections.

A,B and L represents Albite, Bytownite and Labradorite respectively.

bytownite is slightly more. This gives a clue that during weathering of the feldspars, the labradorite being softer than bytownite weathered fastly into fine particles, becoming difficult to remove. Thus, during washing, some of the coarser particles of bytownite have been easily removed from the clay resulting in a less quantity in the washed sample as shown by the X-ray pattern. On the other hand, the finer particles of labradorite fail to separate and thus came out with the washed clay, resulting in the reduction of bytownite and consequently that of anorthite. It is known that labradorite contains about 32% albite and 64% anorthite whereas bytownite contains 22% albite and 77% anorthite. Thus the removal of a portion of bytownite from the washed clay results in the reduction of anorthite.

Conclusion

On the basis of the results obtained during the mineralogical study of Swat kaolinite, the following conclusions may be drawn:-

1. The kaolinite is feldspathic in origin.
2. Chemical and mineralogical analyses show that the semi-weathered material is in fact a mixture of anorthite, albite, and kaolinite free quartz and mica and the minerals are present in the order cited. The washed material, on the other hand, contains about 50-60% kaolinite the rest being the spars with a little of magnesium silicates.
3. The DTA curves show that the washed sample gives distinctive thermal curve which has been used for the qualitative identification and quantitative estimation of the concentration of kaolinite in the aggregate.
4. X-ray studies indicated the presence of kaolinite in the raw and the washed samples as 15-20% and 45-50% respectively, the rest being mainly the plagioclase feldspars.

5. According to a recent report,¹³ the total reserves are 1.7 million tons. This after beneficiation, comes to about 255 thousand tons containing 50 per cent kaolinite.

6. It may be concluded that the chemical and mineralogical analyses and the differential thermal curves and other data are correlative with the nature of the X-ray diffraction patterns. In the final conclusion, therefore it may be stated that the mineral kaolinite in the raw and the treated samples is poorly crystallized and is between 15-20% and about 50% respectively.

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References

1. S.M. Haque, Private Communications (Geological Survey of Pakistan, 1965).
2. Whyte, Unpublished Report (North Regional Laboratories, P.C.S.I.R., Peshawar, 1965).
3. F.A. Faruqi, Unpublished Work (West Regional Laboratories, P.C.S.I.R., Lahore, 1962).
4. R.A. Shah *et al.*, *A Study of a Swat Kaolinit*, Pakistan J. Sci. Ind. Res., **7**, 18 (1964).
5. H. Bennett and W.G. Hawley, *Methods of Silicate Analysis* (Academic Press, London, 1965).

6. F. Singer and S.S. Singer, *Industrial Ceramics* (Chapman and Hall Ltd., London, 1963), p. 27.
7. F.A. Faruqi and H. Qureshi, *Mineralogy of Ahl Kaolinite*, Pakistan J. Sci. Res., **17**, 4 (1965).
8. F.A. Faruqi, *Mineralogy and Ceramics Investigation on a High Alumina Clay from Skesar Hills*, Pakistan J. Sci. Ind. Res., **9** (1966).
9. E.W. Koenig, J. Am., Ceram. Soc., **25**, 420 (1942).
10. H. Insley and R.H. Ewell, J. Res Nat. Bur. Stds., **14**, 615 (1935).
11. G.W. Brindley and J. Nakahira, J. Am. Ceram. Soc., **42**, 319 (1959).
12. F. Singer and S.S. Singer, *Industrial Ceramics* (Chapman and Hall Ltd., London, 1963), p. 102.
13. A.T. Moosvi, S.M. Haque and M. Muslim, *Geology of Shah Dherai China Clay* (Publications Issue No. 21, June, 1966).