

A STUDY OF A HIGH ALUMINA CLAY FROM MUSAKHEL

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(Received May 31, 1965)

A high alumina clay from Musakhel has been studied for its physico-ceramic properties alongwith the identification of the associated minerals by X-Ray and D.T.A methods. The deposit has been found to contain aluminite, alumite, boehmite and diaspore besides other minerals usually associated with kaolinite. The probable genesis of the deposit has also been discussed.

The results of this investigation show that this clay is the richest of all the clays so far reported to occur in Pakistan in respect of its alumina content of 66.3% (fired basis), thus making it suitable for the manufacture of high alumina and mullite refractories.

Introduction

In order to collect information on Pakistan glass and ceramic raw materials, the West Regional Laboratories, P.C.S.I.R., Lahore, in collaboration with other laboratories has undertaken a comprehensive programme to evaluate the indigenous raw materials. Previous work on the clay resources of West Pakistan has already been reported.¹⁻³

This communication is in continuation of this project and is based on the study of a high alumina clay occurring in village Musakhel at a distance of about 17 miles from Mianwali. This region is particularly rich in secondary clay deposits, a number of which have already been reported.¹⁻²

Representative samples were collected by the authors from the surface out-crops of the seam. The clay occurs in three distinctive bands. The top layer of 4-5 feet. width is white in colour and powdery in texture. The out-crop of the middle portion is about 10 feet. lower than the top layer, is also about 4-5 feet. wide and is of dirty colour, while the lower one is of dull white colour and about 6 feet. high. The deposit is in the form of a regular horizontal seam and has been traced over one mile in length. The approximate reserves are estimated to be half a million tons.

Experimental

Chemical compositions and physical properties namely plasticity, water of plasticity, drying and firing behaviour, specific gravity, particle size distribution, DTA and IRA were determined by methods previously described.^{1,2}

Alkalies were determined on an EEL flame photometer. Cation exchange capacity (CEC) of the samples was determined by the ammonium acetate method as employed by W.E. Worall, *et al.*⁴

Results and Discussion

Chemical Analyses and Mineralogical Studies.—The chemical analyses of the samples is given in Table 1. In addition to the three distinct layers of the deposit, the overburden was also analysed.

The top layer of the deposit (sample No. 2) showed a high loss on ignition which was found to be due to 10.15% SO₃ content. This layer also contained 16.38% acid soluble alumina. Since this layer of the deposit contained a high proportion of a white material, this was selectively removed and analysed (sample No. 6, Table 1). This white portion contains 30.20% alumina of which 29.34% is acid soluble, 23.0% SO₃ and 0.20% of Na₂O. This white portion thus being mainly aluminium sulphate, it was considered

TABLE 1.—CHEMICAL ANALYSIS.

Sample No.	Ignition loss %	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	TiO ₂ %	CaO %	MgO %	Na ₂ O %	K ₂ O %	SO ₃ %	Al ₂ O ₃ (acid % soluble)	Ignition loss at 1100 C. %
1	11.23	62.58	25.08	0.11	0.525	0.46	Minute traces	0.40	0.493	1.34	0.85	12.2
2	35.33	27.09	37.56	0.43	0.16	traces	Nil	—	—	10.15	16.38	57.8
3	14.59	33.08	51.64	0.49	0.24	Nil	„	—	—	0.429	1.10	14.5
4	14.4	43.55	41.42	0.29	0.27	„	„	—	—	Nil	—	14.7
5	14.26	47.90	37.10	0.16	0.28	traces	„	—	—	„	—	14.4
6	63.23	5.46	30.20	0.025	0.20	Nil	„	0.2015	Nil	23.0	29.398	59.9

necessary to make a mineralogical study of the deposit with a view to study its genesis.

Sample No. 1, namely, the overburden is very gritty, consisting of coarse grains and small pebbles of quartz and quartzite upto 5 mm. across in a matrix of a rather hard fine grained clay rock. The X-Ray pattern indicates major amounts of quartz and kaolinite with four additional faint lines suggestive of a minor proportion of alunite, $KAl_3(SO_4)_2(OH)_6$.

The thermogram (Fig. 1) shows peaks at 594°C. and 956°C. characteristic of kaolinite. The small peak at 775°C. in conjunction with the small endothermic peak at 532°C. can be identified as alunite. Kaolinite completely masks the presence of quartz. The kaolinite content is estimated at 41% and on this basis the aluminite may be about 12%. However, on the basis of 0.493% K_2O and 0.4% Na_2O the calculated amount of alunite and natro-alunite is 4.4% and 5.195%, respectively.

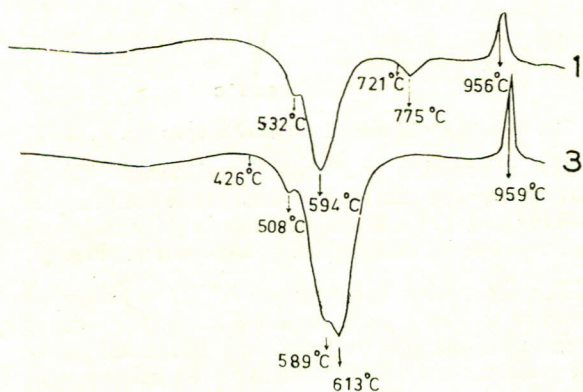


Fig. 1.—Differential thermal curves of samples No. 1 and 3.

The top layer of the clay deposit (sample No. 2) is a fine grained buff grey clay rock cut by numerous irregular veins and layers upto 1 cm. in thickness of a white crystalline material which as discussed later has been identified as aluminite, $Al_2(SO_4)(OH)_4 \cdot 7H_2O$.

The large compound endotherm in (Fig. 2) between 100-245°C. is due to the dehydration of aluminite in stages which produces individual peaks at 163° and 245°C. with possibly an intermediate stage at 214°C. A small exothermic reaction at 829°C. is interrupted by a large endothermic peak at 910°C. signifying the dissociation of $Al_2(SO_4)_3$. Kaolinite is identified by the endothermic peak at 569°C. and the estimated content is about 18%. The weight loss after

heating to 1100°C. is approximately 58%, which is consistent with the estimated kaolinite content, and roughly 80% aluminite.

The X-Ray pattern also indicates aluminite and kaolinite as major constituents.

The white portion selected from sample No. 2 (sample No. 6) consists of a high proportion of aluminite and is of comparatively lower specific gravity (1.83). Both the thermogram (Fig. 2) and X-Ray pattern (Table 2) are similar to those of sample No. 2 but the estimated kaolinite content of 11% is distinctly lower and the weight loss on heating (60%) is slightly higher; hence the inference that it contains nearly 90% of aluminite. The X-Ray data of aluminite by Hollingworth *et al.*,⁵ is also given in Table 2 for comparison.

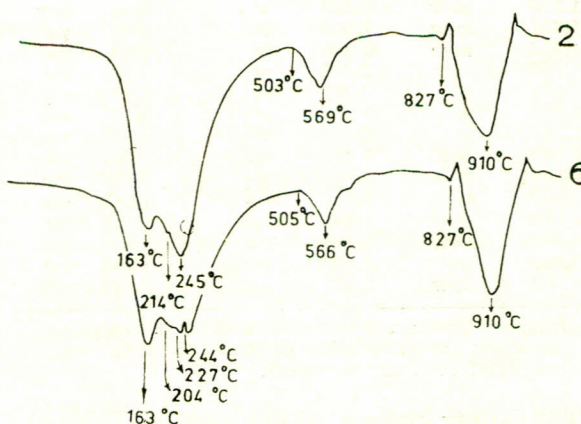


Fig. 2.—Differential thermal curves of samples No. 2 and 6.

The middle layer of the deposit (sample No. 3) is a pale fawn grey clay rock, rather hard and very fine grained.

The thermogram (Fig. 1) is characterised by a compound endotherm with peak at 589°C. and 613°C. indicating a mixture of kaolinite and boehmite. The smaller peak at 508°C. is almost certainly due to diaspore. The estimated kaolinite content calculated from the 959°C. peak by comparison with the corresponding peak area of sample No. 4 and 5 which are very rich in kaolinite is 44%. Accepting this value as correct the corresponding boehmite content is 42%. The diaspore content is probably about 8% bringing the estimated total to 94%. The water content of such a mixture would be 13.7% whereas the weight loss on heating to 1100°C. is 14.5% suggesting thereby the estimated kaolinite and boehmite content may both be slightly low.

TABLE 2.—X-RAY POWDER DATA.

Sample No. 3, Boehmite		Sample No. 6, Aluminite		Aluminite 6	
d(A°)	I	d(A°)	I	d(A°)	I
6.122	vs	9.03	vs	9.0	s
3.158	s	7.921	vs	7.8	s
2.340	s	6.400	m-s	6.33	ms
1.981	w	5.505	m	5.4	m
1.858	m-s	5.281	w	5.2	vw
1.844	m	5.014	m-s	4.96	m
1.764	w	4.762	m-s	4.7	ms
1.658	m	4.221	m very broad	4.18	mb
1.524	m-w	3.727	vs	3.72	s
1.449	m	3.455	m	3.54	vw
1.432	m	3.350	m-w	3.41	m
1.394	vw	3.193	m-w	3.31	w
1.381	m	3.106	m-w	3.16	w
1.307	m	3.033	m-w	3.06	mw
1.204	vw	2.881	w	3.01	mw
1.175	m-w	2.715	m	2.86	w
1.158	m-w	2.627	w	2.68	mw
1.131	m-w	2.509	w	2.60	vw
1.112	m-w	2.406	w	2.49	vw
1.090	vw	2.343	w	2.38	vw
1.044	w	2.213	m	2.32	vw
1.025	w	2.150	w	2.19	mw
1.018	w	2.098	w	2.13	vw
0.989	vw	2.063	vw	2.08	vw
0.0981	v-vw	1.987	m	2.048	vw
0.949	m-w	1.923	vw	1.960	mw
0.0930	m-w	1.892	vw	1.908	vw
0.0923	m-w	1.859	vw	1.879	vw
0.909	w	1.830	vw	1.840	vw
0.902	m-w	1.797	vw	1.810	vw

vs, very strong; s, strong; m-s, moderate to strong; m, moderate; m-w, moderate to weak; w, weak; vw, veryweak; vvw, very very weak.

The X-Ray pattern of this sample (Table 2) indicates major quantities of kaolinite and boehmite with a faint indication of probably diasporé; quartz was not detectable.

The bottom layer of the deposit (sample No. 4 and 5) is a compact, fawn grey clay rock, very fine grained rather similar to sample No. 3.

The thermogram (Fig. 3) of sample No. 4 is an excellent one of kaolinite with a slight endothermic depression at 117°C. indicating 1 or 2% of absorbed water. The estimated kaolinite content based on comparison with a standard kaolinite is 90% in case of sample No. 4 and 92% in case of sample No. 5. These are probably under-estimated.

The X-Ray pattern of these samples reveals only kaolinite.

Infra-red Absorption Analysis.—The infra-red absorption analysis of all the samples of the deposit was done in order to obtain any additional useful information.

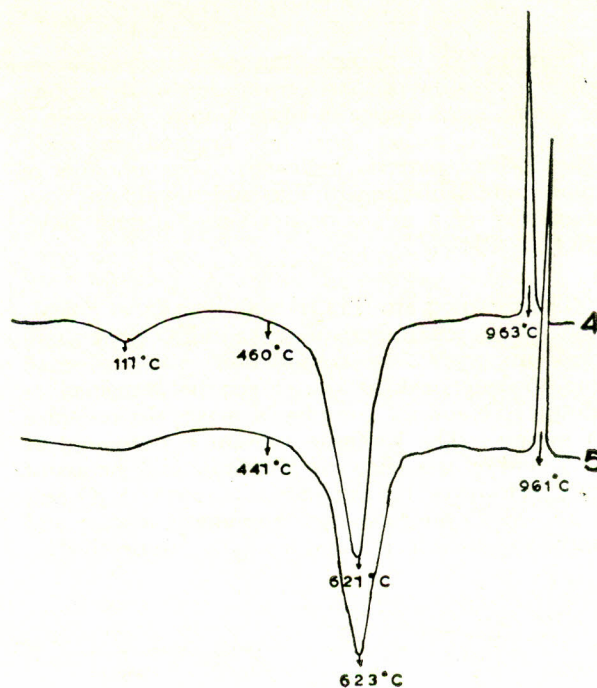


Fig. 3.—Differential thermal curves of samples No. 4 and 5.

The absorption spectrogram of sample No. 4 and 5 are typical of kaolinite and confirm the X-Ray and DTA findings. For brevity only one spectrogram (of sample No. 5) is shown in (Fig. 4).

The absorption spectrogram of the overburden is shown in Fig. 5. Although it is essentially similar to the kaolinite spectrogram, two additional peaks are evident; one well defined at 2.85 micron and the second broad peak between 14.5 and 15 micron. The peak at 2.85 micron is presumably due to hydrogen bonded hydroxyl groups in alunite and the broad peak between 14.5 and 15.0 micron is due to the sulphate ion of alunite which has been shown to be present in the overburden. Hunt, *et al.*⁶ have already pointed out that the absorption peak at about 15 micron is due to sulphates.

The attempt to obtain absorption spectrograms of aluminite and other constituent layers of the deposit did not produce satisfactory results due to the solubility of some of the phases present.

Further work involving a modification of the separation method is in progress and the results will be reported separately.

Cation Exchange Capacity.—The CEC of the samples is given in Table 3. The CEC of samples

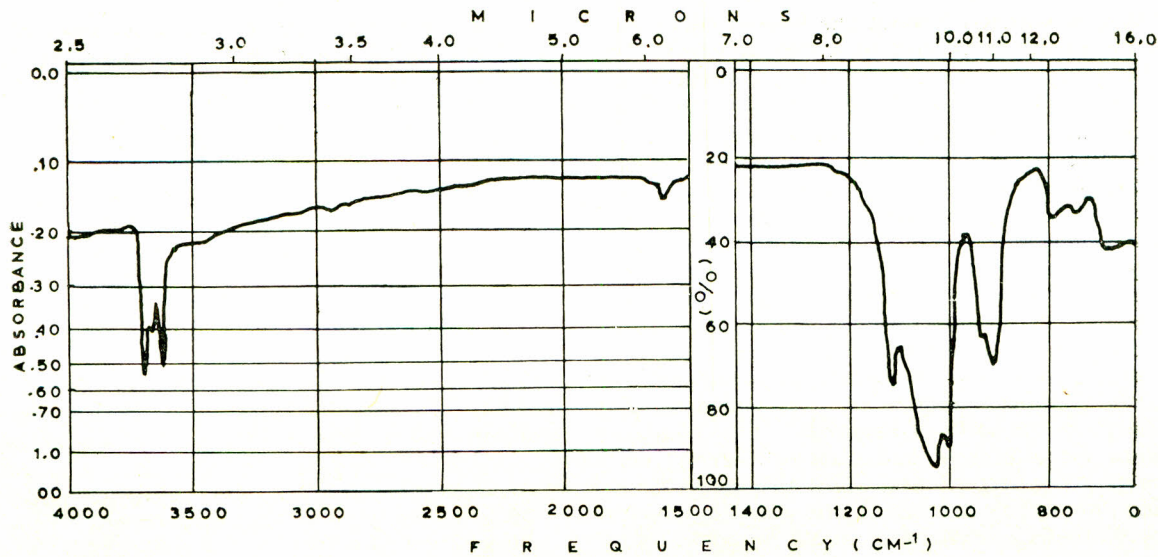


Fig. 4.—Infrared absorption curve of sample No. 5.

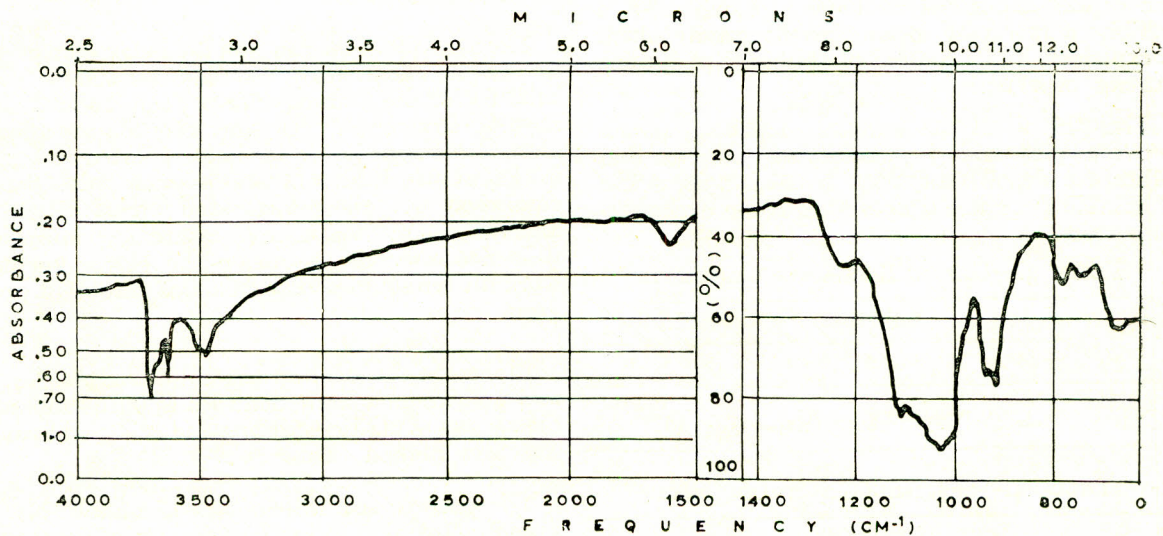


Fig. 5.—Infrared absorption curve of sample No. 1.

No. 4 and 5 which have already been identified as kaolinites fall within the normal range namely 7-15 m.e./100 g. The value for sample No. 4 (7.6 m.e./100 g.) indicates that it is a better ordered clay as compared to sample No. 5 (12.1 m.e./100 g.). Sample No. 3 has a higher CEC (14.8 m.e./100 g.). This may be attributed to the presence of diaspore, HAlO_2 , in which the hydrogen is exchangeable.

Before the CEC of the sample No. 2, namely the top layer of the deposit is discussed it would be

well to remember that it is a mixture of kaolinite and aluminite which according to mineralogical examination occurs in the approximate ratio of 1:4. Aluminite, $\text{Al}_2(\text{SO}_4)_3(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ contains four OH ions and apparently should possess no exchangeable cations. However, the selected white portion from the top layer (sample No. 6) which has already been identified as aluminite gives a CEC value of 12.5 m.e./100 g. It thus appears that its behaviour is similar to the case where the hydrogen of the exposed hydroxyl are replaceable by a cation.⁸ Such hydroxyl groups

would be exposed around the broken edges analogous to the behaviour in a clay mineral. The CEC value of sample No. 2 is comparatively lower at 7.9 m.e./100 g. due to the presence of kaolinite. This lowering of the CEC can possibly be due to the presence of well ordered kaolinite although it is difficult to make any definite comments on this behaviour. It, however, appears that the clay content of the representative sample contains large amounts of kaolinite as compared to the sample subjected to the mineralogical examination. On the basis of the chemical analysis (Table 1) and on the assumption that all the sulphate content is present in the form of aluminite and the excess alumina, other than that which is acid soluble, in the form of kaolinite. The calculated values for aluminite and kaolinite are 43.68% and 51.04%, respectively. This also agrees closely with the silica content of the sample which is approximately the same as would be taken up by the kaolinite content.

The specific gravity of the various sections of the deposit are given in Table 4. Sample No. 2 exhibits a markedly lower specific gravity which is explained by its content of aluminite of specific gravity of 1.83.

The pH of all the samples (Table 4) ranges between 4.21 and 5.45 indicating thereby that either the deposit has been exposed to the acidic surroundings or it has hydrogen as the exchangeable cation.

TABLE 3.—CATION EXCHANGE CAPACITY.

	Sample Nos.					
	1	2	3	4	5	6
C.E.C. m.e./100 g.	—	7.9	14.87	7.6	12.13	12.5

TABLE 4.—SPECIFIC GRAVITY AND pH.

	Sample Nos.					
	1	2	3	4	5	6
Specific gravity	2.561	2.178	2.685	2.54	2.49	1.837
pH	5.19	4.25	4.67	4.75	5.45	4.21

TABLE 5.—CERAMIC PROPERTIES.

Sample Nos.	Water of plasticity%	Drying shrinkage%	Firing shrinkage %	Fired colour at 1000 C.
4	20.97	5.0	8.3	Creamish white
5	18.71	5.0	8.3	White

Ceramic Properties.—A representative mixture as at present being mined shows the following chemical analysis:

I/L	43.93%
SiO ₂	17.95%
Al ₂ O ₃	37.22%
Fe ₂ O	0.07%
CaO	0.71%
MgO	0.18%

The high loss on ignition is due to the presence of aluminium sulphates in the top layer of the deposit. This is, however, advantageous as on ignition the clay product gives the following analysis, (fired basis):

Al ₂ O ₃	66.3%
SiO ₂	31.98%
Fe ₂ O	0.13%
CaO	1.28%
MgO	0.32%
Calculated PCE			+38

The analyses of the raw and fired clay show it to be an excellent high alumina refractory clay suitable for the manufacture of high alumina and mullite refractories. No other clay of such a high alumina content has so far been reported to occur in Pakistan. Initial laboratory-scale trials have confirmed the above-mentioned views. In view of the high sulphate content, however, it is necessary to precalcine the clay. Further work on refractories based on this clay is in progress.

In view of the low iron content of samples No. 4 and 5 which have been identified as pure kaolinite, their water of plasticity drying and firing behaviour was also studied (Table 5).

The particle size distribution of samples No. 3 4 and 5 are plotted in (Fig. 6). In view of the sulphate content in the overburden and the top layer, their particle sizes were not determined.

The particles upto 10 micron in all the three samples studied ranged between 50-60% indicating thereby that the clays are well crystallized. The large amount of coarser particles also appears to agree with the lower drying and firing shrinkage of samples No. 4 and 5. Although these samples do not contain any sulphate they crack on firing thus necessitating a blend with ball clay or any plastic clay for ceramic uses.

Genesis of the Deposit.—Basic aluminous sulphates like alunite and aluminite are usually

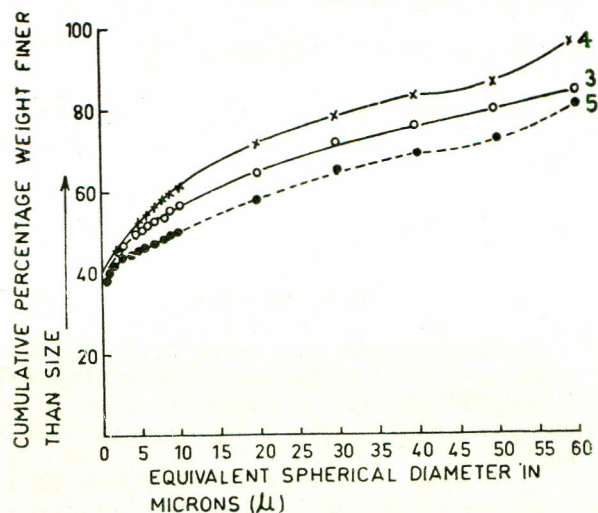


Fig. 6.—Grain size distribution of samples No. 3, 4 and 5.

found to be of secondary origin resulting from the action on recent or tertiary clays, marls or lignites by sulphate solution derived by the alteration of marcasite or pyrite on aluminous silicates.⁹ It would, therefore, be of interest to discuss the possible mode of formation particularly of aluminite.

The Musakhel area is particularly rich in secondary clays. In addition, gypsum is found in abundance as also sulphur springs in the vicinity. Alum shales occur in the Salt Range near Kala Bagh in two distinct horizons in the Eocene (nummulitic series and again at the base of the underlying Jurassic series.¹⁰ Pyrites is reported to be disseminated through the Eocene shale in microscopic particles, the proportion of sulphur varying from 2 to 13%. This shale has been used locally for the preparation of alum. Aluminite has also been reported¹¹ to occur at Chittidand in the Salt Range.

In the present case it appears that samples No. 2 to 5 were originally a variable series of kaolinitic and bauxitic clays and that the aluminite and alunite have been formed by the action of infiltrating sulphuric solutions. The sulphuric solutions may originate from any of the sources of sulphur mentioned above. However, it would be difficult to be dogmatic about it without further geological knowledge of the area.

The presence of coarse quartz grit in the overburden (sample No. 1) suggests that it involved a different parent rock type and the finer fractions presumably contained potassium bearing minerals which allowed the formation of alunite.

From the chemical analyses of the samples (Table 1) it is interesting to note that sample No. 3 contains only traces of sulphate whereas it is totally absent in samples No. 4 and 5. It thus appears that the upper layers of the original deposit contained considerable amounts of bauxitic materials which were readily acted upon by the sulphate solutions, further penetration being hindered by the lower layers which are mainly kaolinitic in nature.

Acknowledgement.—The authors are indebted to Dr. E. H. Beard of Overseas Geological Surveys U.K and his colleagues for the X-Ray and some of the D.T.A. work.

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