Clays and Clay Minerals, Vol. 23, pp. 468–472. Pergamon Press 1975. Printed in Great Britain

THE SEPARATION OF ALUNITE IN ALUNITIC KAOLIN BY SELECTIVE FLOCCULATION

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(*Received* 27 *January* 1975)

Abstract—This work describes the separation of alunite from natural alunitic kaolins by applying a selective flocculation procedure. In order to determine the most efficient separating procedure preliminary experiments were performed with artificial mixtures of alunite and kaolin. The same procedure was then applied to natural alunitic kaolin which enabled the preparation of kaolin of considerable purity.

INTRODUCTION

Kaolin deposits in Turkey will not be sufficient to meet the future demand. It is estimated that the need for 1975 will be $1{\cdot}2 \times 10^6$ tons production of which will not be possible from the present deposits D.P.T. (1971). Therefore it is necessary to search for new kaolin deposits and to upgrade the existing deposits.

Turan (1967), has reported the existence of important kaolin deposits in Turkey which contain alunite as an impurity. The author also indicated that these deposits, which cover a large area, are located mainly in the north-western part of Anatolia.

A group of investigators have tried to purify these kaolins by the usual washing procedure but they were not able to obtain satisfactory results. Although sulphate content decreased by heating at 800°C, remarkable changes in clay properties, particularly in plasticity of samples, were observed at high temperature, S.T.R.C., Turkey (1972).

Research related to alunitic clays was reported by Breckett and Williams (1891), Hill (1908), Ross and Kerr (1930), Ransome (1909), Lindgreen (1905) and Knizek and Fetter (1945, 1946, 1950), who devoted their studies mainly to the formation of these clays. Knizek and Fetter evaluated their use as refractory raw materials.

Research related to the removal of alunite from alunitic clays has not been reported in the literature. Therefore we have directed our studies to the removal of alunite from alunitic clays found in Turkey.

EXPERIMENTAL AND RESULTS

In an aqueous medium a process depending on the rheological, physical and chemical properties of one mineral may be affected by the other. Therefore, in this study, we have first investigated the possibility of separating two minerals from each other by using a mixture of two kaolins and one alunite, the properties of which had been determined. Specimens were dried in an oven at 105°C for at least 2 hr and ground to pass a 200-mesh screen. Chemical analysis of these specimens are given in Table 1. Their TGA and DTA curves are shown in Figs. 1 and 2, and X-ray powder diffraction data are given in Table 2. These data indicate that the Merck kaolin and the natural alunite are practically pure materials. The alunite from Seydiköy resembles Utah alunite in its composition.

The chemical analysis of natural alunitic kaolin is given in Table 3. TGA and DTA curves are shown in Figs. 3 and 4, and X-ray powder diffraction data are given in Table 4. These data indicate that alunitic kaolin consists of 70% kaolin, 21·6% alunite, 8% silica and 0·5% residue.

In order to learn the proper pH at which to separate kaolin from the alunite–kaolin mixture by selective flocculation we determined the ξ potential of these substances with a micro-electrophoresis apparatus and a microscope, Yarar, B. (1971). The change in ξ potential of kaolin and alunite as a function of pH are shown in Fig. 5. These curves indicate that the isoelectric point of the kaolin specimens are in the neighborhood of pH 11·6, at which kaolin flocculates. A similar point for the alunite was not observed. The ξ potential of alunite remained unchanged above pH 8·0.

With a self recording balance, Martin (Prolabo—France), the sedimentation curves of alunite and kaolin specimens were recorded for varying pH ranges. Results of these experiments are shown in Figs. 6, 7 and 8.

It is observed that the sedimentation rate of the aqueous suspensions of kaolin specimens exhibit a

Table 1. Chemical analyses of the samples

%	Kaolin (Ko 47)	Kaolin (Merck)	Alunite (Seydiköy)
H_2O	11·85	13·40	13·01
SiO_2	55·20	46·50	0·57
Al_2O_3	31·65	39·10	37·22
TiO_2	0·04		—
Fe_2O_3	0·61	0·76	—
MgO	0·25	—	—
CaO	0·25	0·10	—
Na_2O	0·20	0·04	—
K_2O	0·10	0·15	10·72
SO_3	—	—	38·41
Total	100·15	100·05	99·93

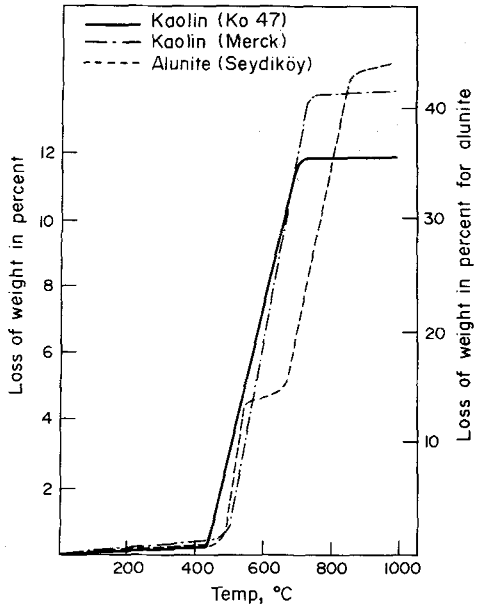

Fig. 1.

continuous decrease up to pH 12. At about pH 12, the sedimentation rate increases sharply (isoelectric point). On the other hand, the sedimentation rate of an aqueous suspension of alunite is not affected significantly by increasing the pH. Hence, the proper pH to separate kaolin from alunite is about pH 11, where clays deflocculate and a large fraction of alunite flocculates (Fig. 9).

It is thus demonstrated that at pH 11 an effective separation can be achieved within the first 1/2–1 hr interval, where the difference in sedimentation rate between kaolin and alunite is at maximum. Although at the end of 4–5 hr alunite settles completely, a significant quantity of kaolin will also be settled by it. Hence the recovery yield of kaolin will decrease. Considerably purer kaolin can be obtained at the end of 1/2–1 hr.

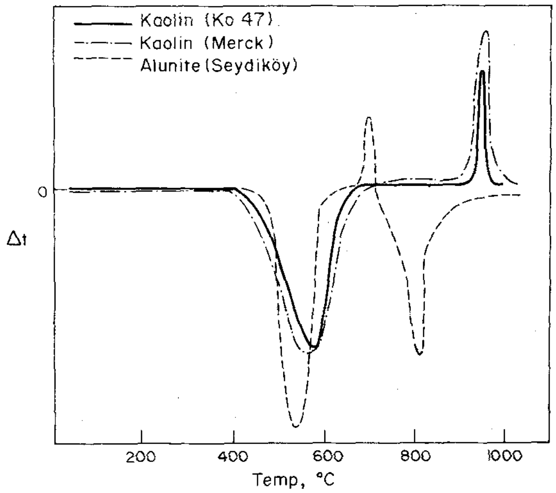

Fig. 2.

Table 2. X-ray diffraction data of the samples

Kaolin (Ko47)		Kaolin (Merck)		Alunite (Seydiköy)	
dÅ	I/I_1	dÅ	I/I_1	dÅ	I/I_1
7·1667	100 k	7·1667	100	5·7166	15
4·4748	37 k	4·4614	32	4·9552	44
4·3744	55 k	4·3532	60	3·4929	30
4·2806	46 q	4·1730	45	2·9882	100
4·1905	51 k	3·8501	26	2·8846	10
4·0492	25 k	3·7384	17	2·4813	5
3·8666	30 k	3·5757	80	2·2896	26
3·7462	20 k	3·4662	45	2·2089	10
3·5899	80 k	2·5565	40	1·9027	32
3·3571	100 q	2·4946	45	1·7460	23
2·9592	10 k	2·3780	40	1·6424	3
2·5707	30 k	2·3411	100	1·5011	12
2·5393	20 k	2·2924	41	2·4935	10
2·5013	32 k	1·9934	25	1·4269	2
2·4610	7 q	1·7890	18	1·3866	4
2·3921	10 k	1·6639	32		
2·3470	40 k	1·6194	15		
2·2980	30 k	1·5417	10		
1·9934	15 k	1·4902	28		
1·8990	10 k				
1·8223	20 q				
1·6667	25 k				
1·6208	8 k				
1·5460	15 k				
1·4902	20 k				
1·3785	10 q				

(k) Kaolinite $Al_2Si_2O_5$–$(OH)_5$.
(q) Alpha Quartz SiO_2.

In order to demonstrate this phenomenon clearly, a series of samples was prepared by mixing kaolin and alunite specimens in varying ratios and mixtures were left to settle at room temperature and at pH 11 for a period of 1/2 hr. Samples were then taken from the flocculated and deflocculated zones and analysed. Results of these analyses are given in Tables 5 and 6. These results indicate that the amount of alunite in the mixture plays an important role in the separation. The amount of alunite mixed with kaolin increases with increasing alunite content. In spite of this, it is evident that the kaolin becomes purer. This observation indicates that with the specimens of high alunite content satisfactory results can be obtained by successive sedimentations of the mixture. The solubility of alunite in such a medium was found to be 1·52%. Therefore the upper fraction was washed out before analysis.

Based on the experimental results obtained with the kaolin–alunite mixtures, purification of Oysu alunitic kaolin was investigated with this procedure.

Table 3. Chemical composition of alunitic clay from Oysu

H_2O	12·55
SiO_2	40·60
Al_2O_3	35·62
Fe_2O_3	0·27
CaO	
MgO	0·12
Na_2O	0·03
K_2O	2·50
SO_3	8·38
Total	100·04

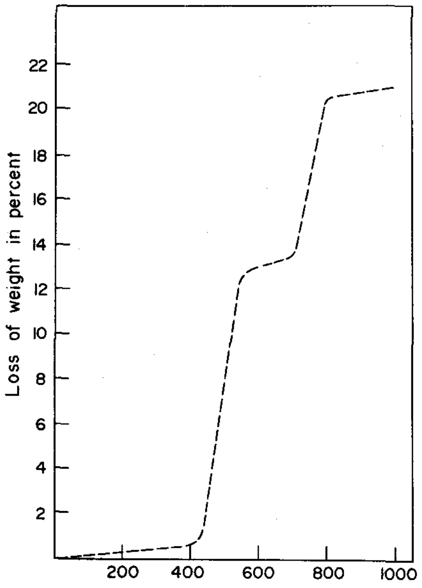

Fig. 3.

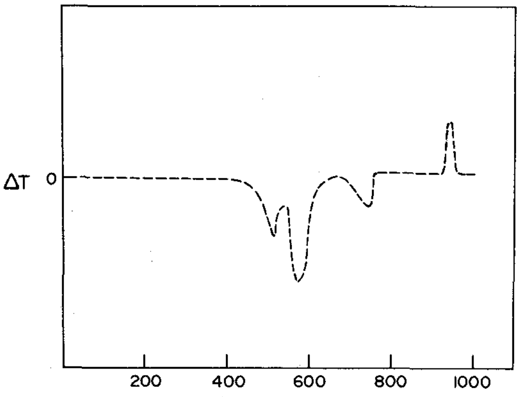

Fig. 4.

Table 4. X-ray diffraction data of the alunitic clay from Oysu

dÅ I/I_1	dÅ	I/I_1	
7·1676	100 k	2·3799	10 k
4·9279	40 a	2·3382	42 k
4·4394	30 k	2·2868	60 a
4·3532	35 k	2·2338	24 a
4·2502	27 q	2·1269	6 q
4·1730	35 k	1·9831	20 k
3·8338	10 k	1·8953	10 k
3·5757	80 k	1·8189	15 q
3·4719	22 k	1·6695	20 q
3·3386	100 q	1·6611	25 k
2·9688	100 a	1·5428	25 k
2·5565	22 k	1·4881	25 k
2·5286	18 k	1·4537	13 a
2·4913	22 k	1·3750	10 q
2·4583	6 q		

(a) Alunite (k) Kaolinite (q) Alpha Quartz

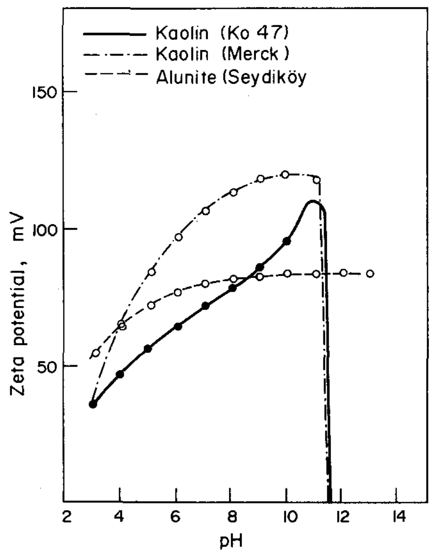

Fig. 5.

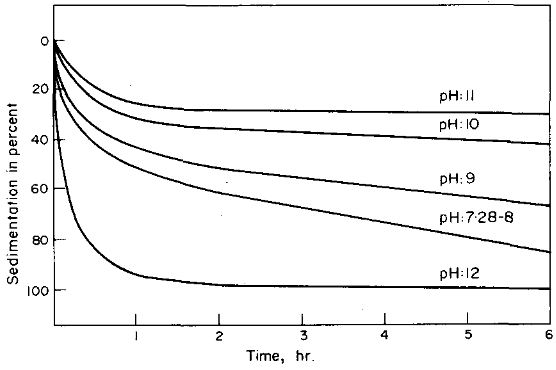

Fig. 6.

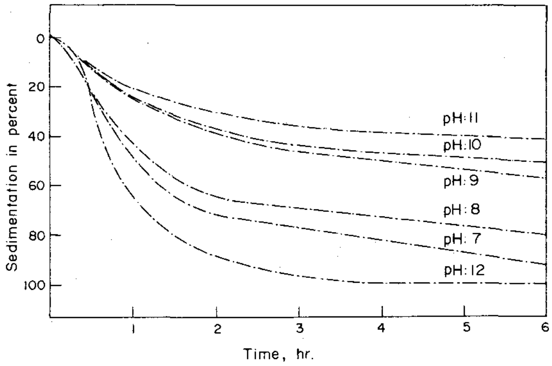

Fig. 7.

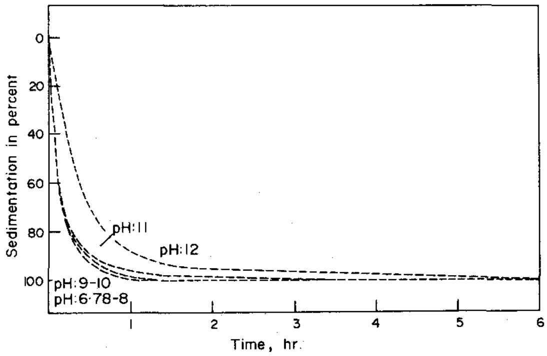

Fig. 8.

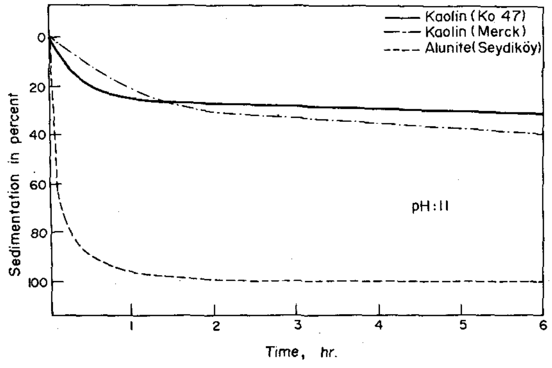

Fig. 9.

At pH 11 and at room temperature sample aliquots were taken from flocculation and deflocculation zones and analysed. The process was repeated three times under identical conditions. Results obtained with the samples taken from the deflocculation zone are given in Table 7. This table shows that the SO_3 content decreased stepwise and finally reached 0·06%. A similar decrease in the alunite content is shown in the same table. The alunite content of the untreated kaolin, 21·68% alunite, exhibited a 5·13% decrease after the first treatment, 1·01% after the second and 0·16% after the third. Hence, it will be possible to purify alunite as a by-product by selective flocculation.

Table 5. Selective flocculation of kaolin (Ko47)—alunite Seydiköy mixtures

Beginning	Comp. of deflocculation region % Alunite	 % Kaolin	Comp. of flocculation region % Alunite	 % Kaolin
% 90 Kaolin (Ko47) % 10 Alunite	1·37	98·63	33·33	66·67
% 80 Kaolin (Ko47) % 20 Alunite	3·03	96·97	52·94	47·06
% 70 Kaolin (Ko47) % 30 Alunite	5·09	94·91	65·85	34·15
% 60 Kaolin (Ko47) % 40 Alunite	7·69	92·31	75·00	25·00
% 50 Kaolin (Ko47) % 50 Alunite	11·11	88·89	81·81	18·19
% 40 Kaolin (Ko47) % 60 Alunite	15·78	84·22	87·09	12·91
% 30 Kaolin (Ko47) % 70 Alunite	22·58	77·42	91·30	8·70
% 20 Kaolin (Ko47) % 80 Alunite	33·33	66·67	94·23	5·77
% 10 Kaolin (Ko47) % 90 Alunite	52·94	47·06	97·59	2·41

Table 6. Selective flocculation of kaolin (Merck)—alunite (Seydiköy) mixtures

Beginning	Comp. of deflocculation region % Alunite	 % Kaolin	Comp. of flocculation region % Alunite	 % Kaolin
% 90 Kaolin (Merck) % 10 Alunite	1·22	98·78	50·00	50·00
% 80 Kaolin (Merck) % 20 Alunite	2·71	97·29	69·23	30·77
% 70 Kaolin (Merck) % 30 Alunite	4·55	95·45	79·41	20·59
% 60 Kaolin (Merck) % 40 Alunite	6·90	93·10	85·71	14·29
% 50 Kaolin (Merck) % 50 Alunite	10·00	90·00	90·00	10·00
% 40 Kaolin (Merck) % 60 Alunite	14·28	85·72	93·10	6·90
% 30 Kaolin (Merck) % 70 Alunite	20·58	19·42	95·45	4·55
% 20 Kaolin (Merck) % 80 Alunite	30·76	69·24	97·29	2·71
% 10 Kaolin (Merck) % 90 Alunite	50·00	50·00	98·00	2·00

Table 7. Selective flocculation of alunitic clay from Oysu

Chemical comp. of alunitic clay	H_2O	SiO_2	Al_2O_3	K_2O	SO_3	% Alunite	% Kaolin
Beginning	12·55	40·60	35·62	2·50	8·37	21·68	70·08
After selective flocculation I	13·20	41·90	37·80	0·58	1·99	5·13	94·87
After selective flocculation II	13·43	45·97	38·87	0·11	0·39	1·01	98·99
After selective flocculation III	13·77	46·26	39·29	0·02	0·06	0·16	99·84

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