

Thermal investigations on alunite and its mixtures with quartz and dickite

M.-A. KASHKAI AND I. A. BABAIEV [M.-A. Кашкай и И. А. Бабаев]

Ulitsa Husi Hadzhieva II, apt. 6, Baku-5, U.S.S.R.

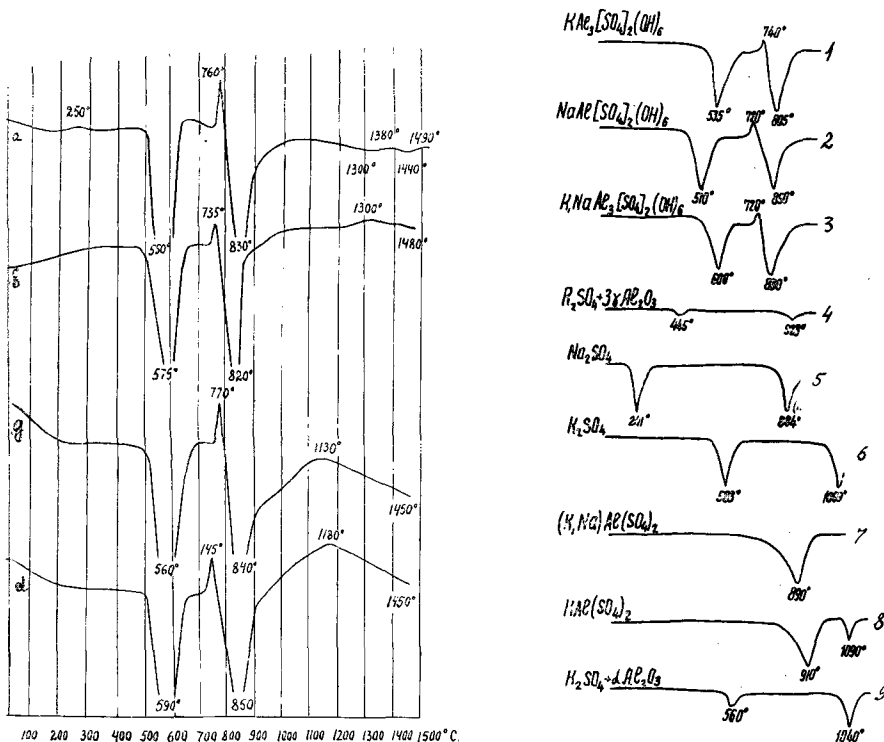
SUMMARY. The thermal decomposition of alunite and of mixtures of alunite with dickite or quartz or both has been studied, and X-ray determinations of the products at various stages of the decomposition have been made. Between 600 and 700 °C the product from alunite is a mixture of anhydrous alum and amorphous alumina; between 700 and 770 °C the anhydrous alum breaks down into aluminium sulphate and alkali sulphate; then in the prominent 850 °C endothermic reaction three-quarters of the sulphate is lost, leaving a mixture of alkali sulphate and γ -alumina. The area of the 850 °C endothermic peak may be used as a measure of the percentage of alunite in alunitized rocks (alunite-quartz-dickite mixtures).

ALUNITE— $R_2SO_4Al_2(SO_4)_3 \cdot 2Al(OH)_6$ —occurs widely in the earth's crust and is a very valuable raw material. Because of this the authors have already carried out extensive studies on this mineral (Kashkai, 1939; Kashkai and Babaev, 1959 and 1960) with a view to assessing reliable methods—both thermal and chemical—for its estimation in alunitized rocks. The best method was found to be by estimation of the SO_3 content by thermal analysis. The second large endothermic peak on the differential thermal curve, at about 850 °C, corresponds to three-quarters of the total SO_3 ; therefore multiplication of the amount of SO_3 indicated by the peak by 1.333 gives the total SO_3 content, which multiplied by 2.546 gives the amount of alunite in the sample. Alunite contents calculated from the alumina, alkali, or H_2O^+ contents of the rock are not so satisfactory because of interference from the other components present. Should sulphides be present in the alunitized rock a correction must be made to the results obtained from SO_3 determination but this is unusual since such minerals are not characteristic of alunitized rocks.

The *thermal decomposition of alunite* has been studied since the early part of the 19th century (Gay-Lussac, 1806; Mitscherlich, 1861; Vinc, 1875; Guyot, 1886; Beggaman and Gullen, 1916; Bowley, 1921; Efendy and Negreev, 1930; Fink, Van Horn, and Pazour, 1931; Dementiev and Lucenko, 1931; Ogburn and Stere, 1932; Alimarin and Podvalny, 1935, etc.) but considerable advances have been made in the past few decades with the more refined apparatus now available (Kashkai, 1939; Asada, 1940; Knizek and Fetter, 1946; Lezar, Krinbill, *et al.*, 1946; Kerr and Kulp, 1948; Gad and Barrett, 1949; Gad, 1950, 1951; Tsvetkov and Valyashinkhina, 1956; Mackenzie, 1957; Kashkai, 1961; Kashkai and Babaev, 1959; Ponomarev, Vereshagin, and Erusalimski, 1963). Typical differential thermal curves for alunite are shown in fig. 1. The curve is a well-defined one and is distinguished by the occurrence of two major endothermic reactions at 480–600 °C and 770–900 °C and also by a well-marked

exothermic peak at 700–70 °C. The high temperature part of the curve, between 1200 and 1400 °C, is characterized by an exothermic reaction yielding a rather broad peak of ill-defined appearance. Differential thermal curves for alunites of different chemical compositions are shown in fig. 2 (curves 1 to 3).

In order to interpret this curve X-ray photographs were taken of alunite heated to various temperatures (table I).



FIGS. 1 and 2: FIG. 1 (left). Differential thermal curves for alunites up to 1450 °C; a, alunite from the Ebeco volcano, Kurile Islands; b, g, and d, alunite from Zaglik, Azerbaidzhan. FIG. 2 (right). Differential thermal curves of alunites, natural and after heating, and of some related products: 1, alunite; 2, natroalunite (almeriite); 3, sodian alunite; 4, alunite heated to 100 °C; 5, Na₂SO₄; 6, K₂SO₄; 7, potassium-sodium alum dehydrated at 400 °C; 8, potassium alum dehydrated at 400 °C; 9, potassium alum heated to 1120 °C.

First endothermic reaction. After heating to 600 °C X-ray diffraction powder patterns were obtained that could be attributed to a mixture of anhydrous K and Na alum. There was no indication of Al₂O₃ lines, confirming the amorphous nature of this oxide. Thus the first endothermic reaction corresponds to the removal of water (6H₂O) from the alunite structure together with a phase transformation to alum according to the reaction.

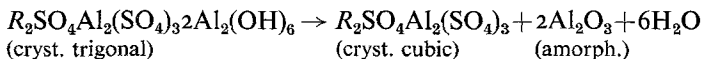


TABLE I. X-ray powder data for natural and burnt alunites,

	Potassium-sodium alunite					Potash and potash-sodium dehydrated alums, artificial	
	Natural	Burnt at				KAl(SO ₄) ₂	(K, NA) Al(SO ₄) ₂
		640 °C	760 °C	800-1000 °C	1000-1400 °C		
<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	
2240 β , 0224 β	1 3.86	6 6.82	1 5.39	2 4.07	3 3.83	3 4.36	2 3.96
2240, 0224, 2134, 3142	4 3.46	4 4.08	2 4.62	3 3.80	3 3.22	4 4.07	9 3.58
2243, 0225, 4041	10 2.96	10 3.67	3 3.99	3 3.67	5 2.91	10 3.67	2 3.10
0006, 0442	2 2.82	1 3.22	10 3.62	6 3.47	1 2.82	1 3.08	8 2.83
4044	3 2.45	9 2.90	2 2.44	3 3.23	7 2.64	2 2.97	3 2.65
0227, 0445, 2461, 2246, 4262	2.27 2.22	3 2.66 8 2.34	7 2.37 2 2.23	6 2.96 8 2.83	5 2.56 4 2.395	8 2.88 1 2.82	3 2.57 9 2.343
0118, 0554, 1562	6 2.107	2 2.26	1 2.086	9 2.54	2.304	3 2.74	1 2.24
0009, 0663, 4047, 4265, 6063	10 1.895 1 1.866	1 1.976 9 1.819	5 1.982 5 1.908	9 2.38 3 2.29	1 2.220 2 2.164	3 2.62 2 2.515	1 2.030 3 1.963
4480, 0448	10 1.750	2 1.714	3 1.840	9 2.092	8 2.094	10 2.377	2 1.907
2249, 2467, 4483, 6281	4 1.649	4 1.446	2 1.438	6 2.004	4 2.027	2 2.278	2 1.885
6284, 4268	4 1.570	7 1.364	4 1.395	3 1.926	3 1.975	2 2.045	9 1.810
0775, 5491, 5385	3 1.539	1 1.317	1 1.838	2 2.015	4 1.925	2 2.015	8 1.779
4486	3 1.477	4 1.274		7 1.741	7 1.773	2 2.985	3 1.661
0.0.0.12	4 1.414	4 1.127		1 1.651	7 1.744	3 1.865	2 1.634
6.4.10.0	6 1.376	4 1.096		10 1.603	10 1.607	9 1.835	1 1.580
	6 1.361	2 1.041		1 1.580	4 1.551	9 1.802	1 1.539
8.2.10.0	4 1.313	2 1.015		4 1.543	7 1.519	3 1.695	10 1.515
	10 1.284	2 0.993		1 1.492	9 1.409	3 1.634	9 1.437
	1 2.247	1 0.952		7 1.435	9 1.378	3 1.599	3 1.410
	8 1.200			8 1.391	10 1.240	5 1.551	10 1.358
	5 1.175			1 1.321	3 1.214	10 1.515	4 1.318
	5 1.107			5 1.248	4 1.192	2 1.484	4 1.296
	3 1.075			3 1.196	6 1.150	7 1.432	5 1.274
	3 1.050			2 1.140	6 1.125	10 1.408	6 1.221
	2 1.031			1 1.116	9 1.097	6 1.329	6 1.209
				6 1.096	7 1.079	4 1.307	7 1.178
				6 1.061	10 1.0423	6 1.270	2 1.160
				5 1.032	3 1.0168	4 1.245	5 1.123
				5 1.010	10 0.9966	6 1.228	2 1.115
				1 0.958		1 1.207	9 1.090
				5 0.916		3 1.198	1 1.078
				3 0.901		8 1.178	3 1.028
				2 0.882		3 1.163	4 1.016
				4 0.8601		2 1.127	4 1.004
				4 0.8321		5 1.117	
						9 1.093	
						5 1.078	
						5 1.028	
						5 1.015	
						5 1.008	
						3 0.990	
						4 0.984	

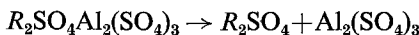
* Tsvetkov and Valyashikhina, 1956.

† Mikheev, 1957.

with data for the compounds formed during burning. Spacings in Å

$Al_2(SO_4)_3^*$	Natural glaserite†	Natural arcanite†	Artificial K_2SO_4	Natural thenardite	Artificial Na_2SO_4	Corundum†	$\gamma-Al_2O_3^*$
$I \quad d$	$I \quad d$	$I \quad d$	$I \quad d$	$I \quad d$	$I \quad d$	$I \quad d$	$I \quad d$
7 5.83	4 7.2	1 5.0	3 4.15	8 4.62	2 5.23	1 3.828	8 3.49
2 4.63	2 5.0	3 4.15	2 3.71	4 3.84	2 5.04	3 3.377	10 2.80
5 3.90	4 3.67	1 3.73	2 3.37	8 3.10	4 4.63	2 (2.805)	10 2.60
10 3.50	1 3.54	1 3.38	2 3.31	10 2.82	2 3.83	2 (2.613)	10 2.55
7 2.95	2 3.47	9 3.00	2 3.19	6 2.63	2 3.50	6 2.573	8 2.38
8 2.66	6 3.18	10 2.88	10 2.99	2.31	2 3.37	4 2.374	10 2.09
5 2.23	10 2.90	1 2.66	10 2.89	2.21	6 3.17	4 2.294	2 1.95
5 2.05	2 2.73	3 2.50	4 2.51	6 2.07	7 3.06	9 2.081	8 1.740
3 1.970	2 2.46	4 2.41	3 2.458	3 1.806	3 2.91	2 (1.915)	2 1.546
3 1.832	2 2.16	5 2.21	2 2.32	2 1.795	2 2.86	3 (1.765)	4 1.510
5 1.764	2 2.06	8 2.08	3 2.238	6 1.664	2 2.77	5 1.738	8 1.405
5 1.659	4 1.84	2 2.00	6 2.06	4 1.598	8 2.63	10 1.592	10 1.375
5 1.538	4 1.77	1 1.94	7 2.00	6 1.542	1 2.559	3 (1.546)	8 1.235
3 1.501	6 1.65	3 1.88	1 1.948	5 1.377	8 2.327	5 1.513	4 1.185
4 1.440	4 1.578	2 1.85	8 1.895	5 1.318	5 2.047	6 1.401	
4 1.410	4 1.541	1 1.76	1 1.872	6 1.293	1 2.00	7 1.374	
5 1.350	2 1.472	2 1.62	2 1.846	4 1.254	2 1.980	4 1.238	
2 1.328	5 1.420	3 1.57	2 1.780	4 1.209	2 1.917	2 1.190	
3 1.287	4 1.363	4 1.440	5 1.698	2 1.191	2 1.835	3 1.146	
5 1.164	2 1.308	2 1.419	5 1.671	2 1.158	8 1.797	2 1.125	
1 1.140	4 1.285	2 1.392	4 1.635	6 1.135	1 1.768	2 1.079	
1 1.068	3 1.05	3 1.350	7 1.572	4 1.096	4 1.707	3 1.043	
6 1.054		1 1.285	1 1.498	6 1.059	8 1.676	5 0.995	
		2 1.245	3 1.483	4 1.043	7 1.662	4 0.933	
		4 1.224	8 1.455	4 1.027	1 1.607	4 0.904	
		1 1.212	7 1.438		1 1.587	3 0.854	
		2 1.141	6 1.429		10 1.551	2 0.843	
		1 1.115	6 1.356		2 1.512	3 0.828	
		1 1.094	6 1.305		5 1.490		
		1 1.048	4 1.287		1 1.459		
		1 1.019	2 1.247		7 1.428		
		1 0.983	7 1.177		2 1.408		
		1 0.965	7 1.147		1 1.372		
			4 1.103		9 1.321		
			6 1.086		9 1.295		
					9 1.278		
					1 1.257		
					1 1.250		
					2 1.231		
					5 1.211		
					1 1.170		
					10 1.132		
					5 1.098		
					10 1.072		
					10 1.064		
					8 1.039		
					8 1.023		

First exothermic reaction. Samples heated to 770 °C yielded powder patterns that could be attributed mainly to K_2SO_4 and $Al_2(SO_4)_3$, although a few lines belonging to K and K-Na alums still remained. No Al_2O_3 lines were observed. The exothermic reaction therefore appears to be due to the decomposition of alum into separate phases.



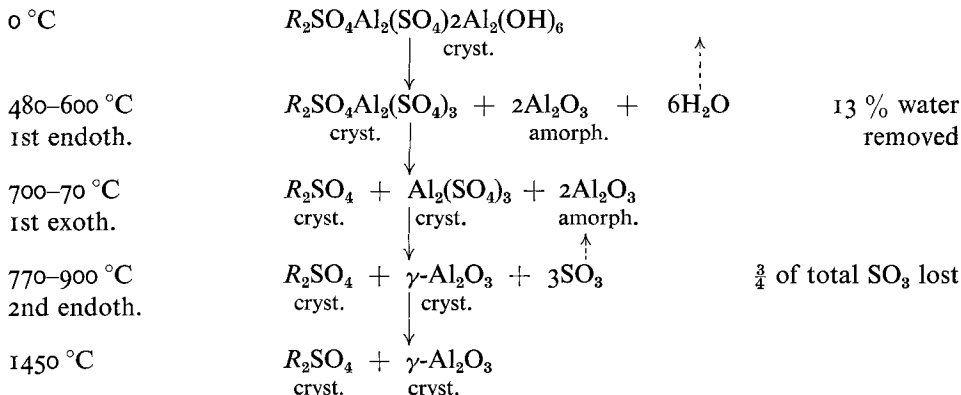
Second endothermic reaction. Powder patterns of samples heated to 900 °C showed that the $Al_2(SO_4)_3$ lines had disappeared whilst lines that could be assigned to Al_2O_3 now became evident. This endothermic reaction is therefore due to the loss of three-quarters of the sulphate present—by the emission of SO_3 —together with the formation of crystalline Al_2O_3 , observed on the X-ray diagram.



After calcining at 1000 °C, the residue showed two reversible endothermic peaks at 445 °C and 923 °C, and after calcining at 1120 °C, at 560 °C and 1040 °C. Since no weight changes were observed these correspond to polymorphic transitions in the product (fig. 2, curves 4 and 5).

Reactions above 1000 °C. The interpretation of that part of the differential thermal curve above 1000 °C is somewhat complicated. In the literature it is assumed that the remaining sulphate (one-quarter of the total) must decompose and be removed in the form of sulphur trioxide. If this were to occur it is clear that the reaction would be an endothermic one. However our results show a small exothermic reaction within the range 1250–1350 °C. The stability of the alkali sulphate phase is further shown by heating natroalunite to 1200 °C. The X-ray pattern was clearly attributable to K_2SO_4 , Na_2SO_4 , and $\gamma-Al_2O_3$. It may be noted that the chemical properties of the alkali sulphates are such that they should be stable up to their boiling points. Possibly the high-temperature exothermic reaction is due to the partial evaporation of K_2SO_4 and Na_2SO_4 and the small weight loss recorded in this temperature range supports this interpretation.

The reactions observed in the differential thermal curve of alunite may thus be summarized:



These phase transformations are illustrated by the X-ray data in table I.

Mixtures of alunite, quartz, and dickite

Alunitized rock is generally a mixture of alunite, quartz, and dickite. Experiments were carried out on artificial mixtures of these minerals in order to study their effect on the differential thermal curve of pure alunite described above. In these experiments pure alunite, dickite, and quartz from the Dashkesan group of alunite deposits were

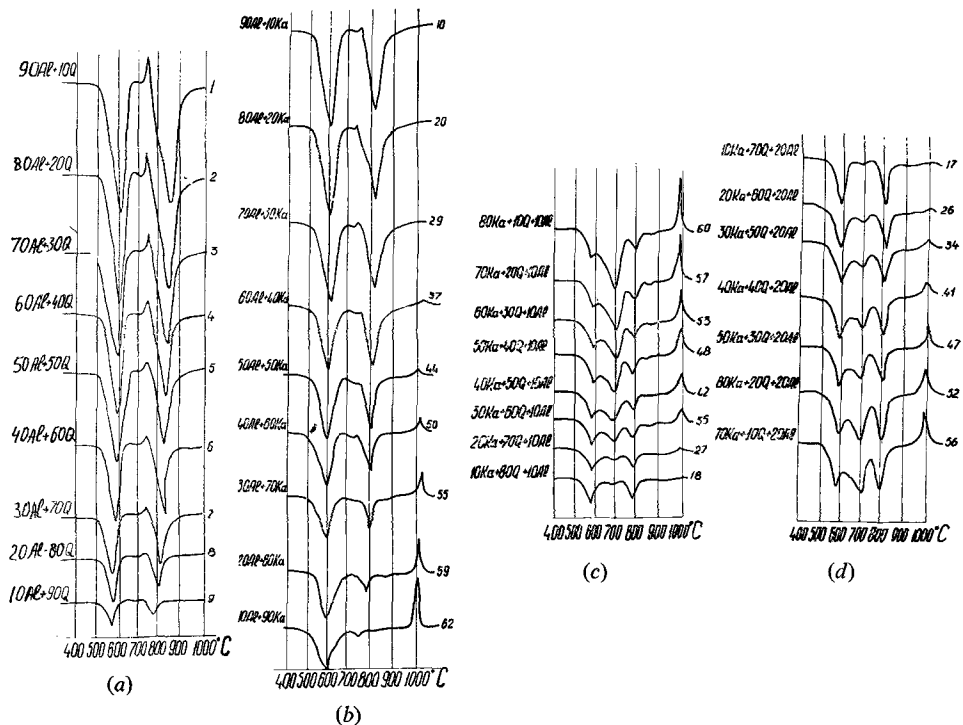


FIG. 3. Differential thermal curves of two-phase and three-phase artificial mixtures: (a), alunite (Al) + quartz (Q); (b), alunite (Al) + kaolinite (dickite) (Ka); (c), kaolinite (Ka) + quartz (Q) + 10% alunite; (d), kaolinite + quartz + 20% alunite.

used. In the differential thermal runs care was taken to standardize particle size (0.1–0.25 mm), sample weight (500 mg), and heating rate (18–20 °C/min). Quartz crucibles and a Pt–Pt/Rh thermocouple were used. All runs were performed at the same sensitivity. It should be added that the thermal reactions of dickite and quartz are well known. Dickite is characterized by an endotherm at 650–700 °C, related to dehydroxylation, and by an exothermic peak at 960–1000 °C. Quartz is thermally inert apart from a small endothermic reaction at 570 °C associated with the $\alpha \rightarrow \beta$ inversion.

Alunite–quartz mixtures. The effect of increasing the quartz content relative to alunite is shown in fig. 3a. The major endothermic peaks gradually diminish in area whilst the reaction temperature also becomes lower. It is clear that in such mixtures

peak areas may be used as a measure of the relative quantities of the two minerals. With a 90% content of quartz the exothermic peak of alunite disappears completely.

Alunite-dickite mixtures. In these mixtures (fig. 3b) the first endothermic peak of alunite and the major endotherm of dickite virtually coincide. When one considers the second major endothermic effect it is clear that with increasing dickite content the peak area diminishes and the reaction temperature decreases from 830 °C to 760 °C. It may also be noted that the exothermic peak of alunite disappears when there is 70% or more dickite present and that the dickite exotherm disappears when there is 70% or more alunite.

Dickite and quartz mixtures with 10 and 20% alunite (fig. 3c and d). Where quartz is predominant in these mixtures, as would be expected, the major reactions for alunite are clearly evident. However, even when the dickite content is increased to 70% the intensity of the alunite endothermic peak remains constant. In these mixtures the exothermic peak of alunite is not observed. When the alunite content is constant at 10% and dickite and quartz at 80–70% and 10–20%, respectively, a further weak subsidiary endothermic peak is noticed. Thus may be due to further loss of SO₃ because of the presence of dickite.

REFERENCES

- ASADA (L.), 1939. *Bull. Inst. Phys. Chem. Res. Japan*, **19**, 976 [M.A. 8–260].
 GAD (G. M.), 1950. *Journ. Amer. Ceram. Soc.* **33**, 208.
 — 1951. *Trans. Brit. Ceram. Soc.* **50**, 328.
 — and BARRETT (L. R.), 1949. *Min. Mag.* **28**, 587.
 [KASHKAI (M. A.)] Кашкай (М. А.), 1939. Труды Азерб. фил. акад. наук СССР (*Proc. Azerbaidzhan Div., Acad. Sci. U.S.S.R.*); Доклады акад. наук СССР (*Compt. Rend. Acad. Sci. U.R.S.S.*), n.s. **24**, no. 9.
 — 1961. Изв. акад. наук СССР, сер. геол. (*Bull. Acad. Sci. U.R.S.S., sér. géol.*) no. 7, 72.
 [— and BABAЕV (I. A.)] — и Бабаев (И. А.), 1959. Изв. акад. наук Азерб. ССР (*Bull. Acad. Sci. Azerbaidzhan S.S.R.*), no. 6.
 KERR (P. F.) and KULP (J. L.), 1948. *Amer. Min.* **33**, 417.
 KNIZEK (Y. O.) and FETTER (H.), 1946. *Journ. Amer. Ceram. Soc.* **29**, 308 and 355.
 LESAR (A. R.), KRINBILL (C. A.), KELLER (W. D., Jr.), and BRADLEY (R. S.), 1946. *Ibid.* **29**, 70.
 MACKENZIE (R.), 1957. *The Differential Thermal Investigation of Clays*. London (Min. Soc.).
 [MIKHЕEV (V. I.)] Михеев (В. И.), 1957. Рентгенометрический определитель минералов. Госгеолизд., Moscow.
 [TSVETKOV (A. I.) and VALYASHIKHINA (E. P.)] Цветков (А. И.) и Вальяшикина (Е. П.), 1956. Труды инст. геол. наук, акад. наук СССР (*Proc. Inst. Geol. Acad. Sci. U.S.S.R.*), **157**.

[Manuscript received November 1966; revised June 1968]