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ARAŞTIRMA MAKALESİ/**RESEARCH ARTICLE**

THERMAL ANALYSIS OF ŞAPHANE AREA ALUNITES AND THEIR PRODUCTS

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ABSTRACT

The thermal properties of Kütahya-Şaphane area alunites and their thermal decomposed derivatives were investigated and chemical composition of alunites were determined. The obtained thermal properties were compared with that of synthetic alunites, which were produced in our laboratory. The optimal decomposition temperature for dissolving of the original alunite and the thermally decomposed alunite was determined.

Key Words: Alunite, Synthetic alunite, Aluminium sulphate, Potash alum, Thermal analysis .

ŞAPHANE BÖLGESİ ALÜNİTLERİ VE ÜRÜNLERİNİN TERMAL ANALİZİ

ÖZ

Kütahya-Şaphane bölgesi alünitlerinin ve alünitten elde edilen ürünlerin termal özellikleri incelenmiş, alünitlerin kimyasal bileşimi belirlenmiş ve laboratuvarımızda üretilen sentetik alünitin termal özellikleri ile karşılaştırılmıştır. Termal bozunmaya uğratılmış alünit ve orijinal alünitin çözündürülmesi için optimum termal bozunma sıcaklığı belirlenmiştir.

Anahtar Kelimeler: Alünit, Sentetik alünit, Alüminyum sülfat, Potas şapı, Termal analiz.

1. INTRODUCTION

Alunite is one of the minerals in jarosite group. It is a basic potassium-alum occuring in rhombohedral crystals (Şengil, 1995; Özacar and Şengil, 1999). Alunite ore which has the formula $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$, forms when volcanic rocks are charged hydrothermally and it occurs with SiO2 minerals (Şengil, 1996) and it contains approximately 50% SiO_2 (Özacar, 2003).

Although pure alunite is colourless, it can be found in different colours such as grey-white, yellowish and red in nature. These colours result from impurities in alunite. Alunite minerals found in different regions can be distinguished from one another in terms of physical properties. For example, specific gravity of China alunite is 2.764 and its hardness is 2 mohs (Ting, 1952) while specific gravity of Şaphane alunite is 1.613 and its hardness is 3.5-4 mohs (Gülensoy, 1968).

Alunite does not dissolve in water and acids in its original form. When it is calcined below 700^oC it dissolves in water and acids (Gülensoy, 1968; Şengil et al., 1987). Alunite gives thermal decomposition reaction products such as Al_2O_3, $Al_2(SO_4)_3$ and K_2SO_4 when it is calcined at 700-750^oC (Gülensoy and Şengil, 1989; Şengil, 1995). Therefore, it has been considered as an important alternative to bauxite for alumina production (Cipriani et al., 1997).

Alunite exists in substantial deposits in Giresun-Şebinkarahisar, Kütahya-Şaphane and İzmir-Foça in Turkey. The deposits in Turkey estimated to be 37 million tones (Şengil, 1995; Özacar, 2003). There is a factory carrying out production of aluminium sulphate and potash alum in Şaphane since 1957 (Şengil and Gülensoy, 1984; Gedikbey, 1985).

In this study, thermal analysis of Şaphane alunite and its products such as $Al_2(SO_4)_3$ and potash alum were carried out. Şaphane alunite were analyzed by using both classic chemical and modern instrumental analysis methods. The thermal decomposition studies were also carried out for alunite and its products. In laboratory conditions, the synthetic alunite was prepared and its thermal analysis were carried out. Thermal decomposition and DTA/TGA curves of alunite and synthetic alunite were compared.

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2. MATERIALS AND METHODS

2.1 Materials

Alunite, aluminium sulphate and potash alum samples used in this study were obtained from Dostel Aluminium Sulphate Ltd. Şaphane-Kütahya, Turkey. Samples were by grinding in laboratory type ball-mill and sieved to give -0.149 mm (100 mesh) size fraction using ASTM standart sieve. All the other chemicals used in the analysis were obtained from Merck Chemical Co.

2.2 Analysis Methods

Analytical weights were taken from stock mineral with the diameter of 0,149 mm and dissolved with NaOH fusion. The analysis of SiO_2, Al_2O_3 and SO_3 from aqueous solution by using classic methods (Gündüz, 1993) and Atomic Absorption Spectrometer (Hitachi 180-70, Japan) were carried out. In addition, chemical analysis of alunite was also made by using XRF instrument (ARL FISON 8400/60). The results obtained from classic methods were compared with that of XRF instrument (Table 1).

Thermal decomposition studies of Şaphane alunite, synthetic alunite, $Al_2(SO_4)_3$ (merck), technical $Al_2(SO_4)_3$ (which is obtained from alunite) and potash alum were carried out by using classic gravimetric method and DTA (Differential Thermal Analysis) / TGA (Thermogravimetric Analysis) instrument (Linseis-L81). The DTA/TGA curves of the samples were taken under atmospheric pressure and reference matter is Al_2O_3. The heating rate in the tests was 10^oCmin^{-1} from 25 to 1300°C.

Synthetic alunite was also produced by the stoichiometric reaction of $Al_2(SO_4)_3$, K_2SO_4 and $Al(OH)_3$. The thermal decomposition and DTA/TGA results of both synthetic alunite and original alunite were also compared.

Thermally decomposed alunite samples and original alunite were dissolved in H_2SO_4 solution and then Al_3+ concentrations in solution were determined by using titrimetric method (Merck, 1982). In order to dissolve alunite in H_2SO_4 solution optimal thermal decomposition temperature of alunite was determined.

3.RESULTS AND DİSCUSSION

Chemical composition analysis results of Şaphane alunite were presented in Table 1.

Table 1. Chemical composition analysis results of Şaphane alunite

Component (%)	Classic method	XRF
SiO_2	43,88	43,47
Al_2O_3	20,35	27,12
K_2O	5,40	5,50
SO_3	21,50	23,05
H_2O	7,40	-
Other components	1,47	0,86

Percentage weight loss of the thermally decomposed alunite and synthetic alunite were determined at different temperatures. These values were given in Table 2 and thermal decomposition curves were shown in Figure 1.

Table 2. Percentage weight loss of Şaphane alunite and synthetic alunite

Temperature	Weight loss (%)		Temperature	Weight loss (%)	
(°C)	Şaphane alunite	Synthetic alunite	(°C)	Synthetic alunite	Şaphane alunite
50	2,32	3,35	**650**	12,39	13,70
100	2,33	4,36	**700**	12,49	17,51
150	2,40	5,64	**750**	20,20	23,42
200	2,39	6,01	**800**	26,22	36,62
250	2,31	8,62	**850**	27,95	39,38
300	2,69	9,14	**900**	29,71	40,54
350	2,57	9,75	**950**	30,18	41,12
400	2,40	11,82	**1000**	30,09	41,28
450	2,55	11,91	**1050**	31,11	41,50
500	3,74	12,93	**1100**	32,30	41,58
550	11,08	12,88	**1150**	32,57	41,74
600	11,70	13,04	**1200**	33,89	42,20

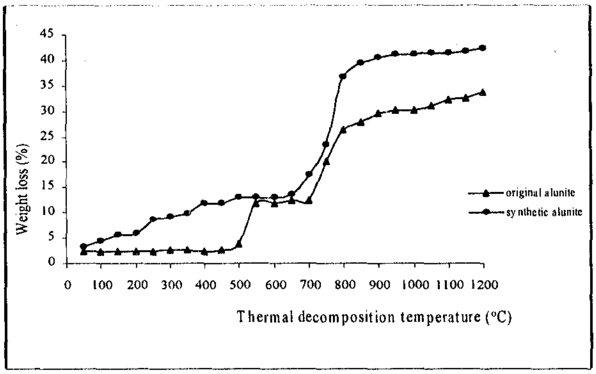

Figure 1. Thermal decomposition curves of Şaphane alunite and synthetic alunite.

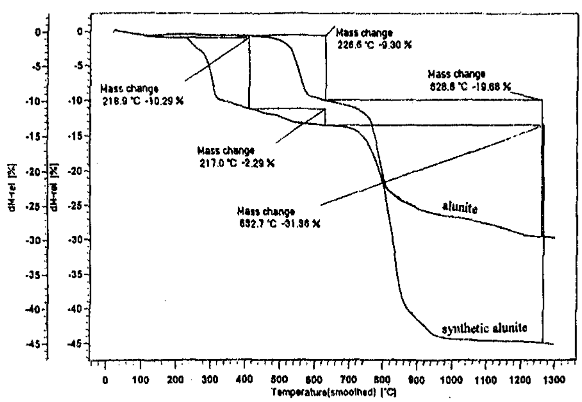

Figure 2. TGA curves of Şaphane alunite and synthetic alunite.

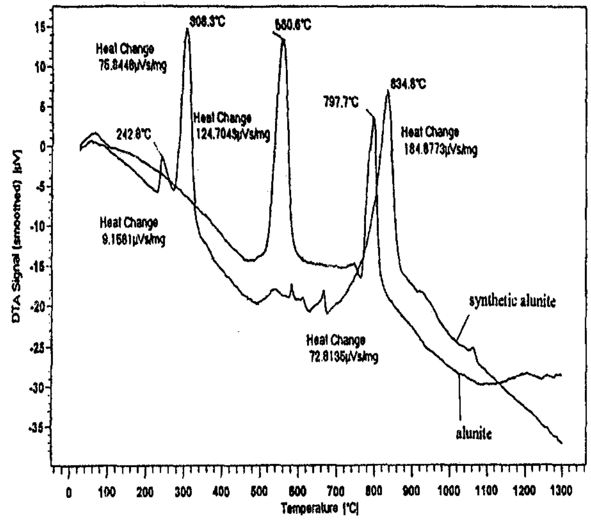

Figure 3. DTA curves of Şaphane alunite and synthetic alunite.

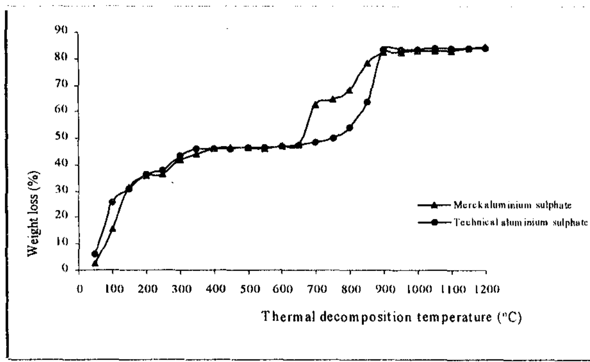

Figure 4. Thermal decomposition curves of Merck and technical aluminium sulphate.

Values of the percentage weight loss of Merck and technical aluminium sulphate at different temperatures were given in Table 3. Thermal decomposition and DTA/TGA curves of these samples were shown in Figures 4 and 5, respectively.

Table 3. Percentage weight loss of Merck and technical aluminium sulphate values at different temperatures

Temperature (°C)	Weight loss (%) Merck $Al_2(SO_4)_3$	Weight loss (%) Technical $Al_2(SO_4)_3$	Temperature (°C)	Weight loss (%) Merck $Al_2(SO_4)_3$	Weight loss (%) Technical $Al_2(SO_4)_3$
50	2,78	6,32	**650**	47,50	47,41
100	15,82	25,89	**700**	62,65	48,30
150	31,33	30,83	**750**	64,54	50,00
200	35,67	36,26	**800**	68,29	54,29
250	36,19	37,94	**850**	78,17	63,84
300	41,99	43,51	**900**	82,44	83,21
350	44,19	45,80	**950**	82,47	83,47
400	45,99	46,09	**1000**	82,85	83,28
450	46,40	46,13	**1050**	82,88	83,68
500	46,54	46,49	**1100**	83,06	83,86
550	46,08	46,72	**1150**	84,07	83,73
600	46,89	46,96	**1200**	84,20	83,85

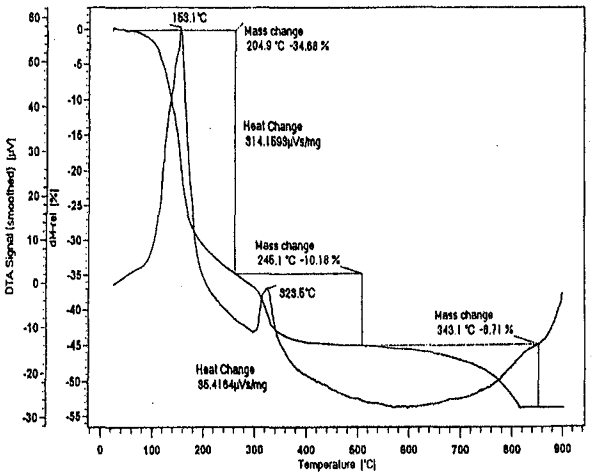

Figure 5. DTA and TGA curves of technical aluminium sulphate.

Values of the percentage weight loss of potash alum produced by DOSTEL Aluminium Sulphate Ltd. were presented in Table 4. Thermal decomposition and DTA/TGA curves of potash alum obtained by using the values in Table 4 were shown in Figures 6 and 7, respectively.

Table 4. Percentage weight loss of potash alum at different temperatures

Temperature (°C)	Weight loss (%)	Temperature (°C)	Weight loss (%)
50	8,85	**650**	48,04
100	33,46	**700**	49,17
150	38,55	**750**	53,56
200	45,70	**800**	59,31
250	45,63	**850**	71,83
300	46,56	**900**	72,27
350	46,78	**950**	72,41
400	46,76	**1000**	72,27
450	46,90	**1050**	72,31
500	47,00	**1100**	72,58
550	47,15	**1150**	72,44
600	47,89	**1200**	72,53

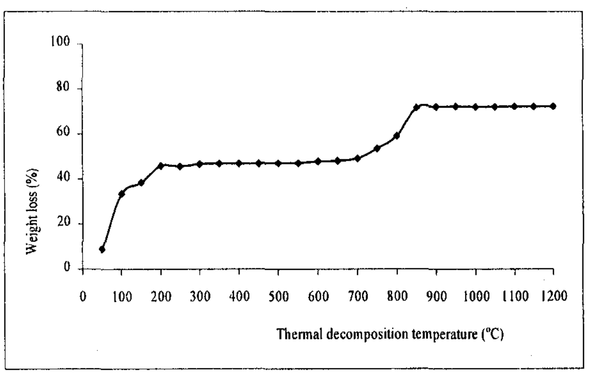

Figure 6. Thermal decomposition curve of potash alum.

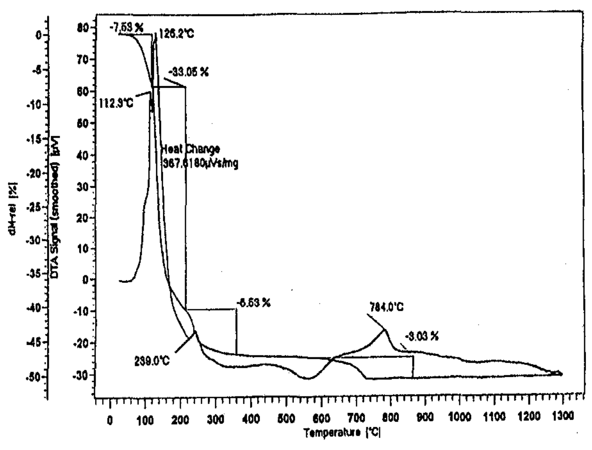

Figure 7. DTA and TGA curves of potash alum.

The percentage of alumina passing into sulphuric acid solution at thermal decomposition temperatures were given in Table 5 and Figure 8, respectively.

Table 5. The percentage of alumina passing into sulphuric acid solution at thermal decomposition temperatures

Thermal decomposition temperature (°C)	Amount of alumina (%)
Original alunite	68,40
100	69,16
200	69,76
300	82,62
400	86,50
500	88,28
600	91,47
700	90,18
800	98,90
900	98,85
1000	98,88
1100	96,74
1200	98,13

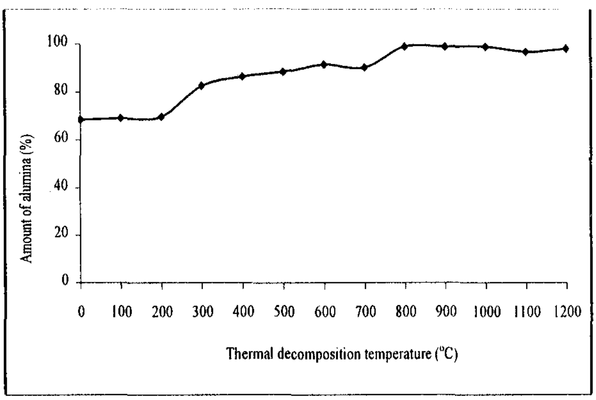

Figure 8. The percentage of alumina present in sulphuric acid solution at different thermal decomposition temperatures.

Chemical analysis results presented in Table 1 indicated that Şaphane alunite was not pure and contained high portions of SiO_2 (43,88 %).

As seen in Table 1, Figures 1, 2 and 3, original alunite has lost its weight at three different temperatures. These are between 450-600°C, 650-900°C and 1100-1250°C. The first endothermic reaction corresponds to complete dehydroxilation of alunite. Mineral was transformed into crystalline $KAl(SO_4)_2$ (alum) and amorphous Al_2O_3 (Kashkai and Babaev, 1969). Alunite used in this study decomposed by losing its structural water at 450-600°C according to the following reaction;

$$Al_2(SO_4)_3.K_2SO_4.4Al(OH)_{3(s)} \xrightarrow{450\text{-}600^{\circ}C} Al_2(SO_4)_3.K_2SO_{4(s)} + 2Al_2O_{3(s)} + 6H_2O_{(g)} \quad (1)$$

The second endothermic reaction refers to the partial desulphatization of alunite by decomposition of alum and loss of ¾ sulphate as SO_3 (Piga, 1995; Itaya et al., 1996; Kashkai and Babaev, 1969). This reaction was observed at 650-900°C.

$$Al_2(SO_4)_3.K_2SO_{4(s)} \xrightarrow{650\text{-}900^{\circ}C} K_2SO_{4(s)} + Al_2O_{3(s)} + 3SO_{3(g)} \quad (2)$$

Lastly, K_2SO_4 decomposes to yield K_2O and SO_3 at between 1100 and 1200°C according to the following reaction.

$$K_2SO_{4(s)} \xrightarrow{1100\text{-}1200^{\circ}C} K_2O_{(s)} + SO_{3(g)} \quad (3)$$

The first and second endothermic reaction of synthetic alunite occured at 100-500°C and 650-900°C, respectively. But third endothermic peak can not be seen clearly in Figures 1, 2 and 3. Although same amount of original alunite and synthetic alunite were used in thermal decomposition and DTA/TGA studies, the weight loss values of synthetic alunite were found to be higher than the original alunite's in the first and second areas of the curves. This is an expected result since original alunite wasn't pure and contained 43,88 % of SiO_2.

Thermal decomposition curves of both Merck and technical aluminium sulphate showed significant weight losses at 50-400°C and 650-900°C (Figure 4). Weight losses observed at between 50-400°C is the direct result of gradual lose of crystal water present in aluminium sulphate. As can be seen in DTA/TGA curves of technical aluminium sulphate (Figure 5), significant amount of crystal water (16 mole) was lost up to 300°C followed by losing further 2 mole of crystal water at 300-400°C. It is concluded from these results that Merck and technical aluminium sulphate contained 18 mole of crystal water. Technical aluminium sulphate produced by DOSTEL Aluminium Sulphate Ltd. has similar thermal properties to that of Merck aluminium sulphate.

Thermal decomposition and DTA/TGA curves of potash alum produced by DOSTEL Aluminium Sulphate Ltd. were shown in Figure 6 and 7. Observation made from these curves indicated that lose of crystal water from alum occured at between 50 and 250°C while lose of SO_3 from aluminium sulphate occured at between 600 and 850°C, but expected decomposition of potassium sulphate at between 1100 and 1300°C did not occur.

The percentage amount of Al_2O_3 passing into sulphuric acid solution from alunite at different thermal decomposition temperatures are given in Figure 8 and Table 5. This curves indicated that the percentage amount of Al_2O_3 accumulating in sulphuric acid solution is directly proportional with the thermal decomposition temperature up to 800°C in the production of $Al_2(SO_4)_3$ from alunite. It reached maximum point at 800°C with 98,90 % yield. Over 800°C the percentage Al_2O_3 accumulating in sulphuric acid solutions decreased gradually. The reason is the portional sinterization taking place over 800°C. Therefore, decomposing alunite at about 750 and 800°C will be sufficient enough for the production of aluminium sulphate.

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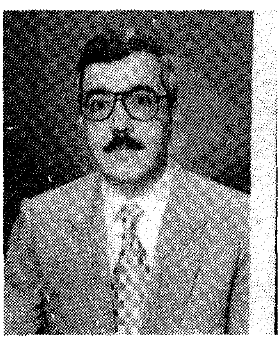

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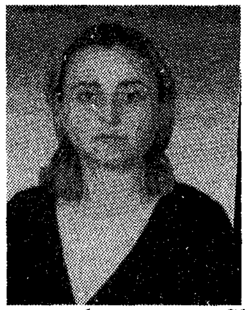

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