NON-ISOTHERMAL KINETIC STUDY ON THE DEHYDRATION OF MECHANICALLY ACTIVATED ALUNITE

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ABSTRACT

In this study, alunite ore was activated mechanically in an attritor for 15 min and then thermal analysis was carried out on both non-activated and activated alunite in different heating rates. Using of thermogravimetry data, the dehydration kinetics of alunite was studying with KAS (Kissenger-Akahira-Sunose) equation. The effect of mechanical activation on the dehydration kinetics of alunite and its thermal behaviour were investigated.

Keywords – alunite, dehydration, mechanical activation, non-isothermal kinetic

MEKANİK AKTİVE EDİLMİŞ ALUNİTİN DEHİDRATASYONU ÜZERİNE İZOTERMAL OLMAYAN KİNETİK ÇALIŞMASI

ÖZET

Bu çalışmada, alunit cevheri bir atritörde 15 dakika süreyle aktive edilmiş, daha sonra farklı ısıtma hızlarında hem aktive edilmemiş hem de aktive edilmiş alunitin termal analizleri alınmıştır. Termogravimetrik data kullanılarak, alunitin dehidratasyon kinetiği KAS (Kissenger-Akahira-Sunose) denklemiyle incelenmiştir. Alunitin dehidratasyon kinetiği ve termal davranışı üzerine mekanik aktivasyonun etkisi araştırılmıştır.

Anahtar Kelimeler – Alunit, dehidratasyon, mekanik aktivasyon, izotermal olmayan kinetik

1. INTRODUCTION

Alunite is one of the minerals of the jarosite group. It is a potassium-alum occuring generally in rhombohedral and hexagonal crystals. Its chemical formula is $KAl_3(SO_4)_2(OH)_6$, and as a source of alum, potassium and aluminum, it is a commercial raw material for the chemical industry. In Turkey, alunite reserves are located in Şebinkarahisar-Giresun (15-20 million tons), Şaphane-Kütahya (7 million tons) and Foça-Izmir (5 million tons) regions [1-3].

The structure of alunite contains aluminium sulphate and potassium sulphate, both of them dissolve in water. However, alunite does not dissolve in water, acids and bases unless calcined. Alunite calcined at temperatures over 500°C dissolves due to the decomposition of the structure. It is widely used in the manufacturing of aluminium sulphate, potassium alum, alumina and potassium sulphate. The ore calcined at 600-650°C is converted to the above mentioned products by acidic and basic extractions. At one of the production method of alumina from alunite, the ore is calcined at 600-650°C and extracted with sulphuric acid. After leaching the solid part is calcined. This calcine is extracted with hot water to remove the soluble potassium sulphate. The remaining solid is obtained as alumina [4,5].

The mechanical activation of minerals makes it possible to reduce their decomposition temperature or causes such a degree of disordering. The mineral activation leads to a positive influence on the leaching reaction kinetics and to an increase in the measured surface area [6]. Mechanical activation of minerals by intensive grinding is a non-traditional way of influencing the processes in extractive metallurgy. Creation of fine particles, increase in specific surface area and formation of defective structures are among the main factors which accelerate leaching in hydrometallurgy. Some special regimes of grinding cause not only the physico-chemical transformations but also the changes in the chemical compositions of the activated minerals [7].

In this study, non-isothermal kinetic study on the dehydration of both non-activated and activated alunite was investigated.

2. MATERIAL AND METHOD

2.1 Material

Alunite ore used in the study was provided from Dostel Aluminum Sulphate Ltd. in Şaphane-Kütahya, Turkey. It was crushed and ground and sieved to -100 μm size. The chemicals used in the extraction study and in the analysis were obtained from Merck Chemical Co. The chemical analysis of alunite ore is 22.98% Al_2O_3, 4.66% K_2O, 45.56% SiO_2, 18.03% SO_3, 0.61% Fe_2O_3, 0.16% CaO+MgO and 8.00% H_2O [8].

2.2 Experimental Procedure

Mechanical activation of alunite ore was performed in an attritor (stirring ball mill) under following conditions: weight of the sample:10 g, weight of balls: 200 g of stainless steel balls with 5.5 mm in diameter, grinding time: 0 and 15 min, stirring rate: 850 rpm.

X-ray diffraction analysis were performed using a Rigaku Ultima X-ray diffractometer and Cu Kα radiation was used (40 kV, 30 mA). Thermal analysis studies (TG and DTA) was performed using Netzsch RT-1500C TGA/DTA apparatus at different (5°, 10°, 15° and 20 °C/min) heating rates.

2.3. Kinetic Study by Thermogravimetry

Dehydration of solids is the subject of many kinetic studies. It helps to understand the following decomposition mechanism: A(s)→B(s)+C(g).

This is a model-free method, which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates (β). The activation energies (E) can be calculated according to the isoconvertional methods of KAS (Kissenger-Akahira-Sunose), Friedman and Ozawa [9]. In kinetic study of both non-activated and activated alunite, KAS equation was used to determine the activation energy of the dehydration reactions.

The kinetic model of dehydration that occurs in non-isothermal conditions is described by KAS eq. (1),

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE}{Rg(\alpha)}\right] - \left(\frac{E}{RT}\right) \qquad (1)$$

where α is the degree of conversion, β is the heating rate in $K.min^{-1}$, A is the pre-exponential factor in min^{-1}, T is temperature in K, R is the gas constant, E is activation energy in $kJ.mol^{-1}$ and g(α) is the integral form of the f(α), which is the reaction model.

According to the above mentioned equation, the plot of $\ln(\beta/T^2)$ versus 1000/T correspoding to different conversions α can be obtained by a linear regress of least square method. The activation energy (E) can be calculated from the slope of every line with better linear correlation coefficient (r) [9,10].

This method is used to calculate the activation energy of the process without its kinetic mechanism.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction Analysis

The X-ray diffraction analysis of non-activated and activated alunite ore is given in Figure 1. Considering the peaks of non-activated and activated alunite, it can be clearly seen that all diffraction peaks of alunite get shorter after mechanical activation. This is due to the starting of amorphisation in alunite structure. In literature[6,7,11], it was reported that the mechanical activation resulted in the amorphisation of mineral particles. The peaks of SiO_2 is not affected with mechanical activation because of its strong structure.

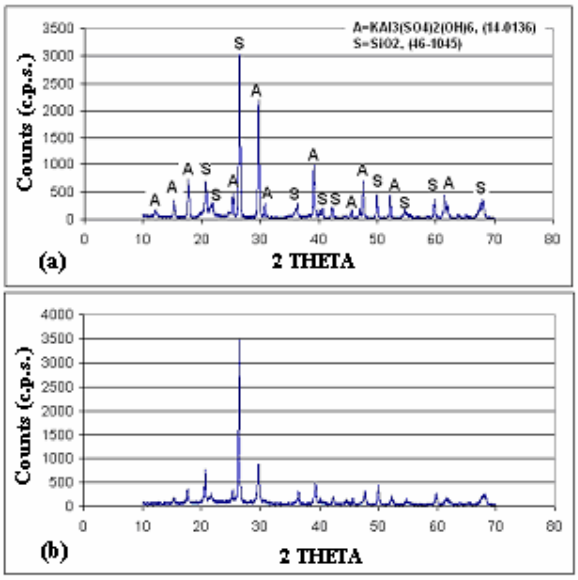

Figure 1. X-ray diffraction patterns of (a) non-activated alunite and (b) activated alunite.

3.2. Thermal Decomposition of Non-activated and Activated Alunite

The thermal analysis (TG and DTA) of non-activated and mechanically activated alunite ore is given in Figure 2. The DTA curves for both alunite ores show two endothermic peak and one small exothermic peak. The first endothermic peaks at about 560°C for non-activated and 545°C for activated alunite ores are strong and sharp. This is due to the dehydration of the structural water and the transformation of alunite into $KAl(SO_4)_2$ and amorphous Al_2O_3, as given in Eq. (2),

$$KAl_3(SO_4)_2(OH)_6 \rightarrow KAl(SO_4)_2 + Al_2O_3 + 3H_2O \quad (2)$$

The exothermic peaks at about 787°C for both alunite ore appear immediately before the second endothermic peak at about 820°C for non-activated alunite ore and 810°C for activated alunite ore.

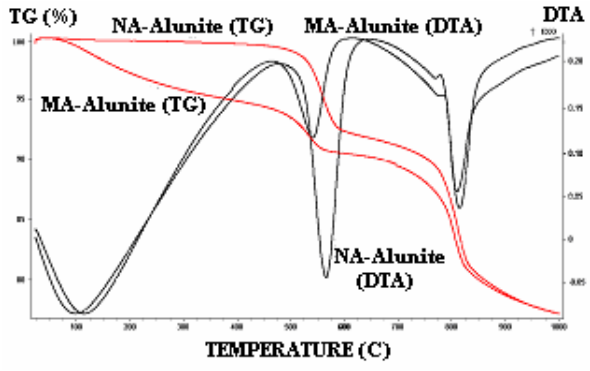

Figure 2. Thermal analysis (TG and DTA) of non-activated (NA-alunite) and activated alunite (MA-Alunite)

It was stated [4] that this small exothermic peak at about 787°C was probably caused by the recrystallization of $KAl(SO_4)_2$ into $K_3Al(SO_4)_3$ and $Al_2(SO_4)_3$, as given in Eq. (3),

$$2KAl(SO_4)_2 \rightarrow \tfrac{2}{3}K_3Al(SO_4)_3 + \tfrac{2}{3}Al_2(SO_4)_3 \quad (3)$$

The second endothermic peak at 820°C for non-activated alunite ore is due to the desulphation by which $K_3Al(SO_4)_3$ and $Al_2(SO_4)_3$ decompose into K_2SO_4 and Al_2O_3, as given in Eq. (4) and Eq. (5),

$$\tfrac{2}{3}K_3Al(SO_4)_3 \rightarrow K_2SO_4 + \tfrac{1}{3}Al_2(SO_4)_3 \quad (4)$$

$$\tfrac{2}{3}Al_2(SO_4)_3 \rightarrow \tfrac{2}{3}Al_2O_3 + 2SO_2 + O_2 \quad (5)$$

The TG curve for non-activated alunite ore shows two steps of weight losses corresponding to the two endothermic peaks. The weight losses are about 8% for the first endotherm (dehydration) and about 22% as the total weight loss after the second endotherm (desulphation). On the contrary, the dehydration of mechanically activated alunite ore is started from 100°C. This is result of amorphisation and structural disordering, providing with mechanical activation. The weight loss up to 650°C is about 8% for activated alunite ore. The mechanical activation affected importantly on dehydration behaviour of alunite ore.

The dehydration temperature decreases about 15°C in mechanically activated alunite ore. The most important point about the dehydration of mechanically activated alunite is its starting from 100°C, due to amorphisation and structural disordering in alunite. In a previous study[11] it was investigated the effect of time of mechanical activation on the thermal decomposition of alunite ore and it was observed that 15 min of mechanical activation is enough to active the alunite ore.

3.3. Non-isothermal Kinetic Study

For the dehydration kinetic study of non-activated and activated alunite, their TG datas were used in non-isothermal conditions. The dehydration part of non-activated alunite is given in Figure 3 and that of activated alunite in Figure 4. According to TG data, α (degree of conversion or ratio of dehydration) and related temperature values (K) were listed in Table 1. ,

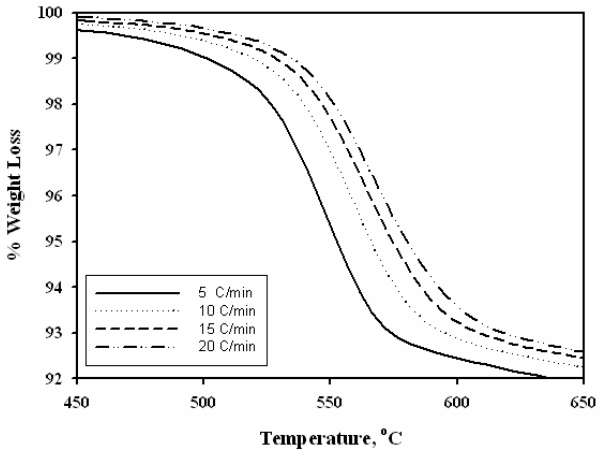

Figure 3. TG curve of non-activated alunite

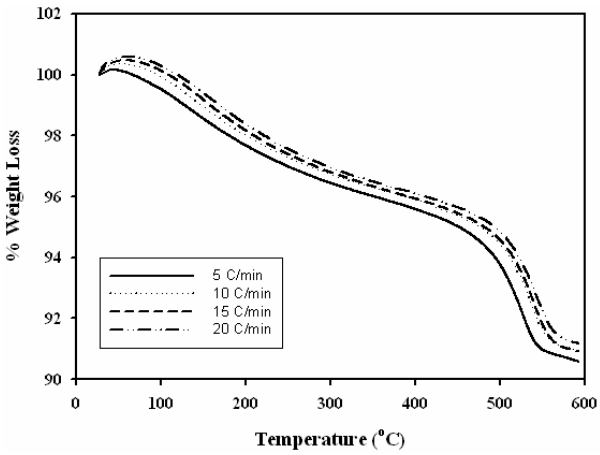

Figure 4. TG curve of activated alunite

According to the equation(1), the plots of $\ln(\beta/T^2)$ versus 1000/T correspoding to different conversions α are given in Figure 5 for non-activated alunite and in Figure 6 for activated alunite. The activation energies (E) were calculated from the slope of every line and regression coefficients were listed in Table 2.

As seen from Table 2, the activation energy values of deydration reaction of non-activated alunite are varying between 173.5 and 303.9 kJ/mol, corresponding to different conversions. These values for activated alunite are varying between 41.16 and 278.29 kJ/mol. In literature, such a relationship between activation energy and degree of conversion was stated [12,13]. It can be said that the activation energy of dehydration reaction of non-activated alunite is about 280-300 kJ/mol.

On the contrary, the activation energy values are varying in wide ranges. The comparison of the activation energy values for non-activated and activated alunite is given in Figure 7.

Table 1. α and T(K) values for different heating rates

	Temperature (K)							
	Non-activated alunite				Activated alunite			
	Heating rate(β, K/min)				Heating rate(β, K/min)			
α	5	10	15	20	5	10	15	20
0.1	764.6	785.2	796.1	801.6	393.6	413.6	424.2	435.3
0.2	792.6	806.8	814.2	819.3	442.0	456.1	466.0	477.9
0.3	804.5	817.1	824.1	828.7	488.6	511.1	518.7	531.3
0.4	811.9	824.5	831.7	836.4	556.9	587.8	594.3	610.7
0.5	818.1	831.1	838.6	843.5	652.1	691.1	694.3	713.4
0.6	823.9	837.4	845.5	851.1	731.1	754.4	760.1	771.1
0.7	830.1	844.5	853.8	860.2	766.3	783.7	788.2	794.9
0.8	842.6	853.9	864.9	872.6	784.7	800.1	803.9	809.9

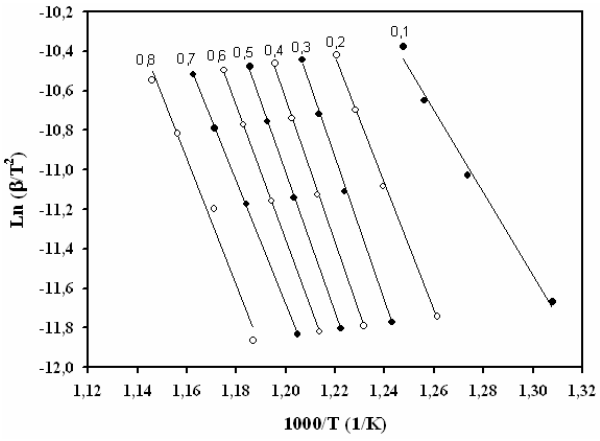

Figure 5. The plots of $\ln(\beta/T^2)$ versus 1000/T correspoding to different conversions α for non-activated alunite

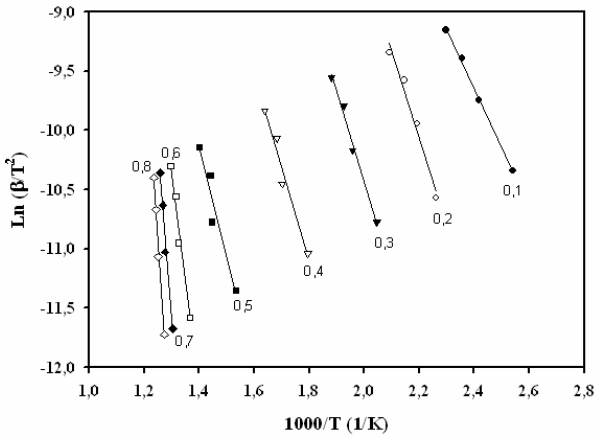

Figure 6. The plots of $\ln(\beta/T^2)$ versus 1000/T correspoding to different conversions α for activated alunite

Table 2. Activation energies (E) and r values for non-activated and activated alunite.

	Non-activated alunite		Activated alunite	
α	E (kJ/mol)	r	E (kJ/mol)	r
0.1	173.5	0.9916	41.16	0.9971
0.2	267.8	0.9982	61.09	0.9781
0.3	302.1	0.9988	63.17	0.9845
0.4	303.9	0.9992	64.41	0.9648
0.5	297.6	0.9993	76.10	0.9301
0.6	282.6	0.9999	152.24	0.9755
0.7	258.8	0.9997	233.06	0.9769
0.8	264.3	0.9828	278.29	0.9758

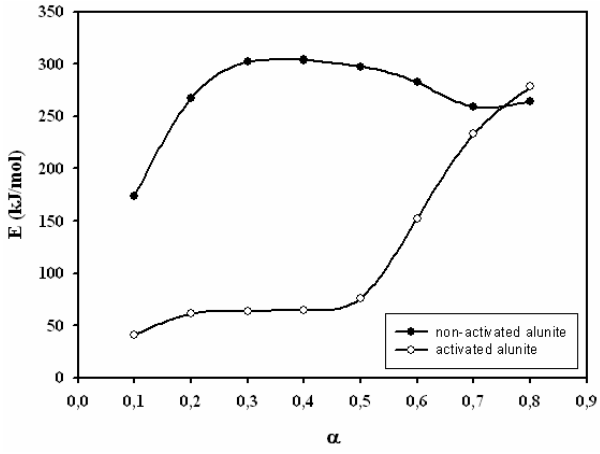

Figure 7. Comparison of activation energies calculated by KAS equation for non-activated and activated alunite

As seen in Figure 7, the activation energy values are in the range of 41 and 76 kJ/mol, up to 0.5 of α. After α=0.5, this value was increased sharply to about 278 kJ/mol. The lower activation energy values of dehydration of activated alunite, up to α=0.5, than that of non-activated alunite is due to amorphization and structural deformation in alunite during the mechanical activation process. It was observed with x-ray diffraction analysis that there was no 100% of amorphization in structure, therefore the activation energy value increased to about 278 kJ/mol.

4. CONCLUSIONS

It was determined with x-ray diffraction analysis that the alunite structure was partially amorphized by mechanical activation.

Mechanical activation affected on temperature range of dehydration reaction of alunite. This reaction occured after 100°C for activated alunite, while it was occured after 450°C for non-activated alunite. This behaviour was supported with TG and DTA.

The dehydration kinetics of non-activated and activated alunite was investigated by non-isothermal method, without kinetic mechanism. The activation energy values of dehydration of non-activated alunite were calculated between 173 and 264 kJ/mol by using of KAS (Kissenger-Akahira-Sunose) kinetic equation. The mechanical activation promoted some amorphization, but not completely, and structural disorders in alunite. This pretreatment decreased the activation energy values to the range of 41-76 kJ/mol, due to amorphization, up to α (degree of conversion)=0.5 and then activation energy was increased to actual values so that there was no 100% amorphization in alunite structure.

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