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The decomposition kinetics of mechanically activated alunite ore in air atmosphere by thermogravimetry

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Abstract

The thermal decompositions of both non-activated and mechanically activated alunite ore have been studied by thermogravimetry (TG). The ore was activated mechanically in an attritor for 15 min and amorphisation in the structure was studied by X-ray diffraction analysis. It can be verified that alunite decomposes in two steps, which are dehydration and desulphation. It was also established that the mechanical activation affected especially on the temperature range of dehydration reaction. The activation energies of dehydration and desulphation reactions have been calculated from the thermogravimetric data at heating rates of 5, 10, 15 and 20 K min^{-1} involving isoconversional methods of Ozawa and Kissenger–Akahira–Sunose (KAS).

Keywords: Alunite; Decomposition; Kinetics; Mechanical activation; Thermogravimetry

1. Introduction

Alunite is one of the minerals of the jarosite group. It is a potassium alum occurring 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 aluminium, it is a commercial raw material for the chemical industry. In Turkey, alunite reserves are located in Şebinkarahisar-Giresun (15–20 million tonnes), Şaphane-Kütahya (7 million tonnes) and Foça-Izmir (5 million tonnes) regions [1–3].

The structure of alunite contains aluminium sulphate and potassium sulphate, both of them dissolve in water. However, it is not soluble 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 products, mentioned above, by acidic [4] and basic extractions [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 [7].Decomposition of solids is the subject of many kinetic studies. In many methods of kinetic estimation, isoconversional method is recommend as trustworthy way of obtaining reliable and consistent kinetic information [8]. It is a ‘model-free’ method, which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates, β. Recently, we have initiated a study of dehydration and desulphation kinetics of non-activated and activated alunite by thermogravimetry. The activation energies are calculated according to the isoconversional methods of Ozawa [9] and Kissenger–Akahira–Sunose (KAS) [10]. In literature there is no report on the thermal decomposition kinetics of mechanically activated alunite. So the aim of the research is to investigate the effect of mechanical activation on the dehydration and desulphation kinetics of alunite.

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2. Experimental

Alunite ore used in this study was provided from Dostel Aluminum Sulphate Ltd. in Şaphane-Kütahya, Turkey. It was crushed, ground and sieved to −100 μm size. The chemicals used in the analysis were obtained from Merck Chemical. The components SiO_2, H_2O, SO_3 and Al_2O_3 in the alunite ore were analysed by gravimetric method. Fe_2O_3, CaO and MgO were analysed by complexometry with EDTA and K_2O was analysed by flame photometry. The chemical analysis of alunite ore is 22.98% Al_2O_3, 4.61% K_2O, 45.56% SiO_2, 18.08% SO_3, 0.61% Fe_2O_3, 0.16% CaO + MgO and 8.00% H_2O.

Mechanical activation of alunite ore was performed in an attritor (stirring ball mill), which is designed and built in our lab, 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 powder diffraction patterns were obtained with a Rigaku Ultima X-ray diffractometer and Cu Kα radiation was used. Thermogravimetric analysis curves were obtained using a Netzsch RT-1500C TGA Instrument in air atmosphere at different heating rates (5, 10, 15 and 20 $K\,min^{-1}$) from room temperature to 1273 K, with 130 ± 2 mg samples. The TG data were used to obtain the apparent activation energies using both Ozawa and Kissenger–Akahira–Sunose (KAS) method.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction analysis of non-activated and activated alunite is given in Fig. 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 partial amorphisation and structural disordering in alunite structure. In literature [6,7], it was reported that the mechanical activation resulted in the amorphisation of mineral particles. Tromans and Meech [11] indicated that mechanical activation resulted in development of large numbers of dislocations and their associated strain fields, which might lead to an overall decrease in long-range lattice periodicity. This may be interpreted as the formation of a metastable "amorphous phase", because line broadening and disappearance of diffraction peaks takes place on X-ray patterns after extended milling.

3.2. Thermal decomposition of non-activated and activated alunite

TG and DTG curves of non-activated and mechanically activated alunite ore are given in Fig. 2(a and b). The DTG curves for both alunite ores show two peaks. The first peak is at about 560 °C for non-activated and 545 °C for activated alunite ores. 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. (1) [12]:

$$KAl_3(SO_4)_2(OH)_6 \rightarrow KAl(SO_4)_2 + Al_2O_3 + 3H_2O \qquad (1)$$

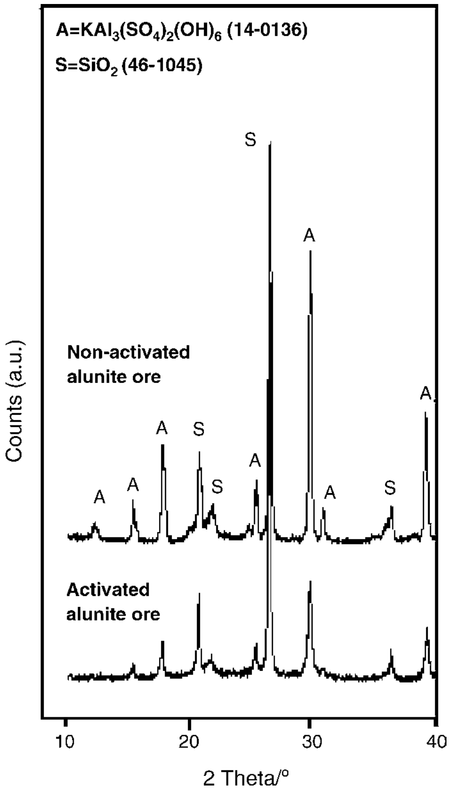

Fig. 1. X-ray diffraction patterns (10–40°) of non-activated and activated alunite.

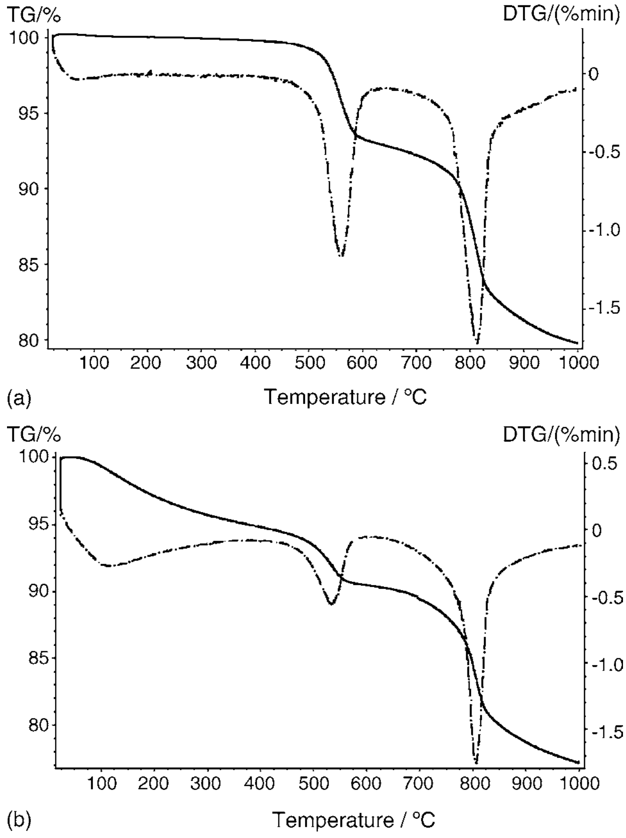

Fig. 2. TG and DTG curves for (a) non-activated and (b) activated alunite.

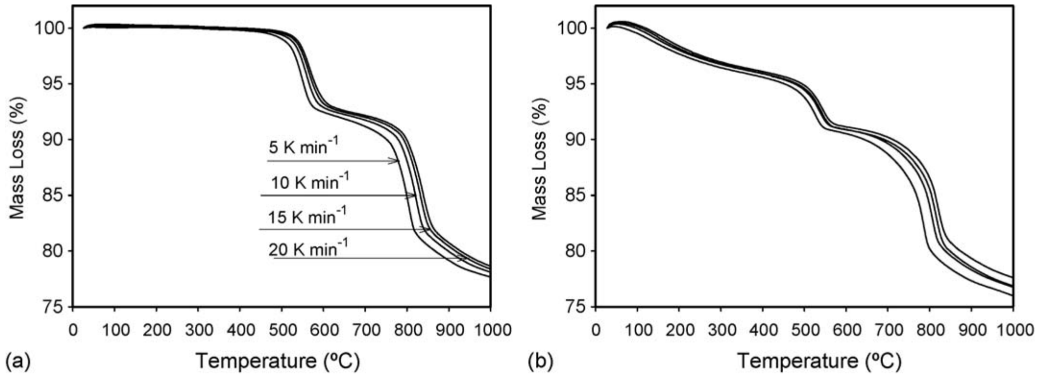

Fig. 3. TG analysis of (a) non-activated alunite and (b) activated alunite at different heating rates.

The second peak is at about 820 °C for both non-activated and activated alunite ore. This is due to the desulphation, as given in Eqs. (2)–(4) [12]:

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

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

$$\tfrac{2}{3}Al_2(SO_4)_3 \rightarrow \tfrac{2}{3}Al_2O_3 + 2SO_2 + O_2 \quad (4)$$

The TG curve for non-activated alunite ore shows two steps of weight losses. The weight losses are about 8% for dehydration and about 22% as the total weight loss after desulphation. In non-activated alunite dehydration takes place at a certain temperature range. This is an expected property for crystalline alunite. However, activated alunite exhibited dehydration reaction starting from 100 °C. This is result of amorphisation and structural disordering, providing with mechanical activation.

3.3. Activation energy of dehydration and desulphation steps

Decomposition 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_α) can be calculated according to the iso-convertional methods. In kinetic study of both non-activated and activated alunite, Ozawa and KAS equations were used to determine the activation energy of the dehydration and desulphation reactions.

The equations used for E_α calculation are:

$$\text{Ozawa equation :}\quad \log\beta = \log\left[\frac{AE_\alpha}{Rg(\alpha)}\right] - 2.315 - \frac{0.4567E_\alpha}{RT} \quad (5)$$

$$\text{KAS equation :}\quad \ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE_\alpha}{Rg(\alpha)}\right] - \left(\frac{E_\alpha}{RT}\right) \quad (6)$$

where $g(\alpha) = \int_0^\alpha f(\alpha)^{-1}\,d\alpha$ is the integral form of the $f(\alpha)$.

At the constant condition of other parameters, the TG curves for dehydration and desulphation of alunite in air atmosphere at various heating rates (β = 5, 10, 15 and 20 K min^{-1}) are shown in Fig. 3 for (a) non-activated alunite and (b) activated alunite. According to isoconversional method, the basic data of α and T collected from Fig. 3(a and b) are illustrated in Tables 1 and 2, respectively.

According to the above-mentioned equations, the plots of log β versus 1000/T and ln(β/T^2) versus 1000/T corresponding to different conversions α can be obtained by a linear regress of least-square method, respectively. The activation energies E_α can be calculated from the slopes of every line with better linear correlation coefficient r. The slopes change depending on the degree of conversion, α, for the dehydration and desulphation

Table 1
α–T data at different heating rates, β (K min^{-1}), for non-activated alunite

α	T (K)							
	Dehydration				Desulphation			
	β = 5	β = 10	β = 15	β = 20	β = 5	β = 10	β = 15	β = 20
0.1	764.6	785.2	796.1	801.6	1017.7	1047.6	1061.5	1069.1
0.2	792.8	806.8	814.2	819.3	1038.5	1061.4	1073.3	1080.1
0.3	804.5	817.1	824.1	828.7	1043.8	1070.3	1081.9	1088.6
0.4	811.9	824.5	831.7	836.4	1055.5	1077.4	1089.1	1095.8
0.5	818.1	831.1	838.6	843.5	1062.9	1083.7	1095.3	1102.1
0.6	823.9	837.4	845.5	851.1	1068.5	1089.2	1100.9	1107.9
0.7	830.1	844.5	853.8	860.2	1073.5	1094.2	1106.1	1113.4
0.8	842.6	853.9	864.9	872.6	1078.1	1099.1	1111.3	1119.1

Table 2
α–T data at different heating rates, β (K min^{-1}), for activated alunite

α	T (K)							
	Dehydration				Desulphation			
	β = 5	β = 10	β = 15	β = 20	β = 5	β = 10	β = 15	β = 20
0.1	393.6	413.6	424.2	435.3	885.1	927.5	932.7	958.6
0.2	442.0	456.1	466.0	477.9	951.1	986.1	997.8	1014.5
0.3	488.6	511.1	518.7	531.3	986.7	1019.2	1031.5	1045.2
0.4	556.9	587.8	594.3	610.7	1011.7	1042.0	1053.3	1065.5
0.5	652.1	691.1	694.3	713.4	1030.0	1057.1	1068.3	1078.6
0.6	731.1	754.4	760.1	771.1	1042.6	1067.5	1078.1	1087.2
0.7	766.3	783.7	788.2	794.9	1050.9	1074.7	1084.9	1093.8
0.8	784.7	800.1	803.9	809.9	1056.9	1080.7	1091.1	1100.4

Table 3
E_α vs. r calculated by Ozawa and KAS methods for non-activated alunite

α	Ozawa method		KAS method	
	E_α (kJ mol^{-1})	r	E_α (kJ mol^{-1})	r
Dehydration				
0.1	177.3	0.993	173.5	0.992
0.2	267.4	0.998	267.8	0.998
0.3	300.1	0.999	302.1	0.999
0.4	302.0	0.999	303.9	0.999
0.5	296.1	0.999	297.6	0.999
0.6	296.1	0.999	282.6	0.999
0.7	281.9	0.999	258.8	0.999
0.8	259.4	0.999	264.3	0.983
Desulphation				
0.1	226.3	0.989	220.7	0.987
0.2	290.7	0.995	288.1	0.994
0.3	271.3	0.987	267.6	0.986
0.4	309.8	0.996	307.9	0.995
0.5	323.4	0.997	322.1	0.997
0.6	325.6	0.998	324.4	0.998
0.7	325.3	0.998	323.9	0.999
0.8	320.3	0.999	318.6	0.999

Table 4
E_α vs. r calculated by Ozawa and KAS methods for activated alunite

α	Ozawa method		KAS method	
	E_α (kJ mol^{-1})	r	E_α (kJ mol^{-1})	r
Dehydration				
0.1	45.7	0.998	41.2	0.997
0.2	65.4	0.983	61.1	0.978
0.3	68.1	0.988	63.2	0.985
0.4	70.4	0.973	64.4	0.965
0.5	83.1	0.946	76.1	0.930
0.6	156.6	0.979	152.2	0.976
0.7	233.9	0.979	233.1	0.977
0.8	277.2	0.978	278.3	0.976
Desulphation				
0.1	128.9	0.956	120.3	0.945
0.2	169.3	0.989	161.8	0.987
0.3	194.7	0.992	187.9	0.991
0.4	220.8	0.992	214.9	0.990
0.5	250.9	0.994	246.4	0.993
0.6	278.3	0.994	275.0	0.994
0.7	293.8	0.995	291.2	0.994
0.8	293.9	0.996	291.1	0.995

reactions of alunite. The α-dependence of the apparent value of E_α, calculated from the slopes of Eqs. (5) and (6) at various α, is shown in Table 3 for non-activated alunite and in Table 4 for activated alunite. As shown in Tables 3 and 4, the activation energies calculated by Ozawa method and KAS method are close to each other.

The activation energy values of dehydration of non-activated alunite were calculated between 173 and 304 kJ/mol by using of KAS kinetic equation. The values calculated by Ozawa method are close to those obtained by KAS method. The mechanical activation promoted some amorphisation, but not completely, and structural disorders in alunite. This pretreatment decreased the activation energy values to the range of 41–76 kJ/mol, up to α (degree of conversion) = 0.5 and then activation energy was increased to actual values. This confirmed the present of crystalline structure of alunite in activated alunite.

The activation energy values of desulphation were between 220 and 325 kJ/mol for non-activated alunite and 120 and 294 kJ/mol for activated alunite. The values calculated by Ozawa and KAS method are also close to each other for desulphation. It can be said that the effect of mechanical activation on desulphation reaction is less than its effect on dehydration of alunite.

4. Conclusions

Alunite decomposes in two steps: dehydration and desulphation. The dehydration of alunite is important for its further treatments. In non-activated alunite, the dehydration reaction starts after about 500 °C. On the contrary, the dehydration of mechanically activated alunite ore was started after 100 °C. Mechanical activation results in amorphisation and structural disordering in alunite. Its effect on desulphation reaction temperature of alunite was not excessive.

For the dehydration and desulphation reactions of non-activated and activated alunite, the activation energies calculated by Ozawa and KAS methods are close to each other. In dehydration of alunite, the activation energies decreased to the range of 41–83 kJ/mol from the range of 173–303 kJ/mol, due to amorphisation and structural disordering, up to α (degree of conversion) = 0.5 and then activation energy was increased to actual values. This confirmed the present of crystalline structure of alunite in activated alunite.

References

[1] H. Gülensoy, MTA Enstitüsü Dergisi (in Turkish) 71 (1968) 93–128.
[2] H. Gülensoy, I.A. Şengil, Kimya ve Sanayii (in Turkish) 31 (157/158) (1989) 116–131.
[3] I.A. Şengil, Turk. J. Eng. Environ. Sci. 15 (1991) 436–446.
[4] M. Özdemir, H. Çetişli, Hydrometallurgy 76 (2005) 217–224.
[5] M. Özacar, I.A. Şengil, Can. Metal. Quart. 38 (4) (1999) 249–255.
[6] P. Balaz, Extractive Metallurgy of Activated Minerals, Elsevier Science B.V., Amsterdam, The Netherlands, 2000.
[7] P. Balaz, E. Boldizarova, M. Achimovicova, R. Kammel, Hydrometallurgy 57 (1) (2000) 85–96.
[8] S. Vyazovkin, C.A. Wight, Thermochim. Acta 340/341 (1999) 53–68.
[9] T. Ozawa, J. Thermal Anal. 2 (1970) 301–304.
[10] H.E. Kissenger, J. Anal. Chem. 29 (1957) 1702–1706.
[11] D. Tromans, J.A. Meech, Miner. Eng. 14 (11) (2001) 1359–1377.
[12] A. Küçük, M.Ş. Gülaboğlu, Ind. Eng. Chem. Res. 41 (2002) 6028–6032.