Effects of mechanical activation on aluminaextraction from alunite ore and its thermal behaviour

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The decomposition and acid leaching has been investigated of alunite ore activated mechanically by grinding in a planetary ball mill in air atmosphere for 0, 15, 45 and 90 min. The mechanical activation appears to decrease dehydration and desulphation temperatures for alunite ore, owing to amorphisation and structural disorders in alunite as examined by XRD, TG and DTA. The highest alumina extraction values from the non-activated alunite ore were y6% by leaching in 1M H_2SO_4 solution for 30 min without calcination and y50% after calcination at 600uC for 1 h, followed by acid leaching under the same conditions. By comparison, for direct acid leaching of mechanically activated alunite ore without calcination, alumina extraction values were y12, 40 and 56% for mechanically activated alunites for 15, 45 and 90 min respectively. These values were y78, 84 and 89% for mechanically activated samples (15, 45 and 90 min respectively) after calcination at 600uC for 1 h and leaching in 1M H_2SO_4 solution at room temperature for 30 min.

Keywords: Alunite, Mechanical activation, Decomposition, Calcination, Leaching

Introduction

Alunite is a mineral from 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 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 which dissolve in water. However, alunite is insoluble in water, acids and bases unless first heat treated in a process called calcination. Alunite which has been calcined at -500uC will dissolve owing 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 600–650uC is converted to the above products by acidic and basic extractions.[4–6]

The mechanical activation of minerals makes it possible to reduce their decomposition temperature causing a high degree of disorder. Mineral activation leads to a positive influence on the leaching reaction kinetics and an increase in the measured surface area.[7] 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 the main factors that accelerate leaching in hydrometallurgy. Some special regimes of grinding cause not only the physicochemical transformations but also the changes in the chemical compositions of the activated minerals.[8]

Extraction studies of alunite in both acidic solutions[6,9] and strong NaOH solution[3] are presented in the literature. In a previous study by the authors,[10] the effect of mechanical activation on the decomposition kinetics of alunite ore was investigated by a non-isothermal method and it was found that the apparent activation energy decreased by mechanical activation. The aim of the present study is to investigate the effect of mechanical activation time on thermal behaviour of alunite ore and alumina extraction in H_2SO_4 solution with or without calcination.

Materials and methods

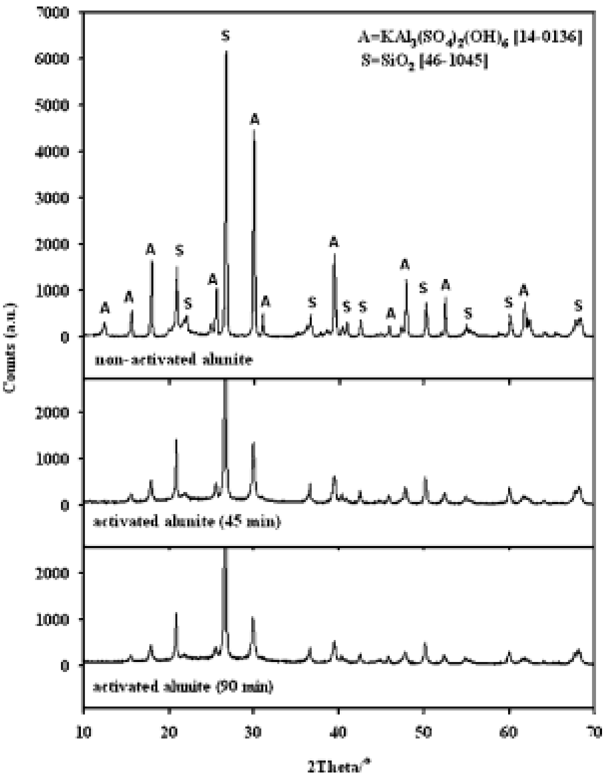
Materials

Alunite ore used in the present study was provided from Dostel Aluminum Sulphate Ltd in Şaphane-Kütahya, Turkey. The ore was crushed, ground and sieved to 2100 *m*m size. The chemicals used in the extraction study and in the analysis were obtained from Merck Chemical. The chemical composition of alunite ore is 22?98Al_2O_3–4?61K_2O–45?56SiO_2–18?08SO_3–0?61Fe_2O_3–0?16(CaOzMgO)–8?00H_2O.

Experimental apparatus and procedure

Mechanical activation of alunite ore was performed in a

Pulverisette 6 planetary mono mill under the following



1 X-ray diffraction analysis of non-activated and activated alunite ores

conditions: the weight of the sample – 10 g, the weight of balls – 200 g of tungsten carbide (WC) balls with 10 mm diameter, grinding bowl – WC (250 mL), grinding time – 0, 15, 45 and 90 min, the speed of main disc – 600 rev min^{21}, grinding process – dry.

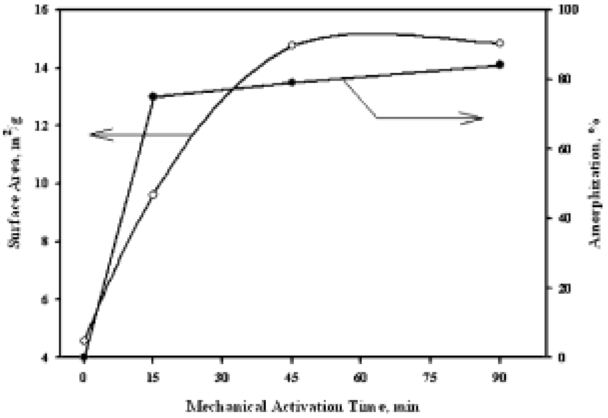
X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and Cu K_a radiation was used. Thermal analysis studies (TG and DTA) were performed using a Netzsch RT-1500C TGA/DTA apparatus. The analysis was carried out at a linear heating rate of 10uC min^{21} up to 1000uC in air, with 100 i 2 mg sample. The surface area was determined by the low temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA).

The degree of amorphisation A of mechanically activated alunite was calculated by the formula[7,8,11]

$$A\sim 1\{\frac{B_0 I_X}{B_X I_0}\ 100\% \qquad (1)$$

where I_0 is the integral intensity of diffraction peak for non-activated mineral, B_0 is the background of the diffraction peak for non-activated mineral, and I_X and B_X are the same values for the mechanically activated mineral. The complementary value, the content of crystalline phase X, is sometimes used instead of the degree of amorphisation A. The relationship is $X5(1002A)\%$.

Calcination experiments were performed in an electrical furnace in air atmosphere at different temperatures (200, 300, 400, 500, 600 and 700uC) for 60 min. Both of the non-activated and activated samples were calcinated and then, leached in 1M H_2SO_4 solution for 30 min at room temperature and a solid to liquid ratio (s/l) of1 : 25. In addition, the samples were leached in the same acidic solution without calcination. All leach experiments were performed at room temperature because of high alumina extractions at this temperature. The higher leach temperature from room temperature has not been needed for increasing of alumina extraction. The leach conditions were the same for all experiments in the present study. The leach conditions and its kinetics for this process are under investigation.



2 Effects of mechanical activation time on surface area and amorphisation degree of alunite

Results and discussion

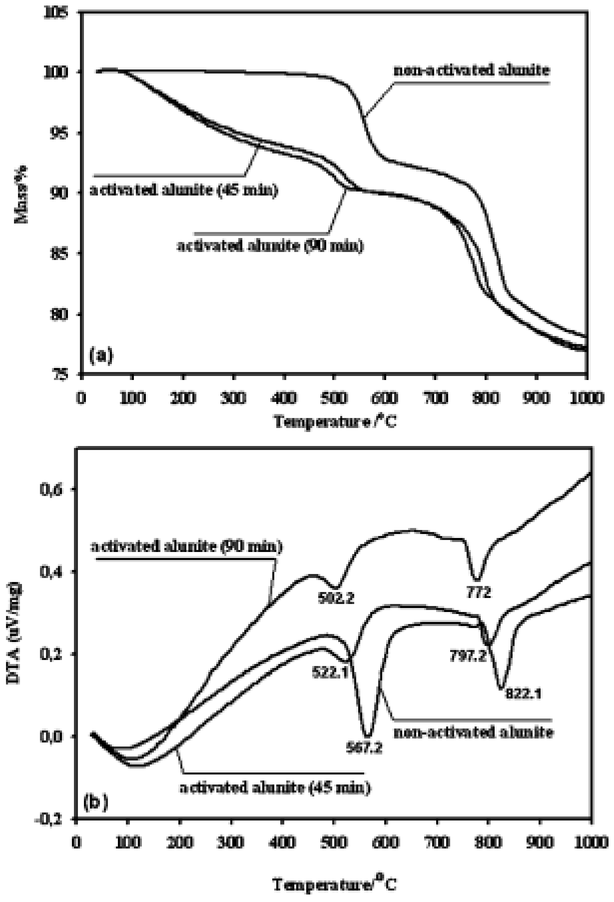
Characterisation of non-activated and activated alunite ores

The X-ray diffraction analysis of non-activated and activated alunite ores is given in Fig. 1. Considering the peaks of non-activated and activated alunites, it can be clearly seen that all diffraction peaks of alunite become shorter after mechanical activation. This is due to the partial amorphisation and structural disordering in alunite. In literature,[7,8] it was reported that the mechanical activation resulted in the amorphisation of mineral particles. Tromans and Meech[12,13] indicated that the mechanical activation resulted in development of large numbers of dislocations and their associated strain fields, which may 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.

As shown in Fig. 2, the specific surface area of the ground particles increases with as much as 45 min of mechanical activation. The lack of increase in this value at 90 min of mechanical activation is a result of recombination of fine grains. This phenomenon has been reported previously in the literature.[8] Because the specific areas do not increase after 45 min of mechanical activation, the degree of amorphisation has predominant influence on the reactivity of alunite after prolonged mechanical activation.

Effects of mechanical activation on decomposition of alunite ore

The thermal analysis (TG and DTA) of non-activated and mechanically activated alunite ores is given in Fig. 3*a* and *b*. The DTA curves for all samples show two endothermic peaks and one small exothermic peak. The first endothermic peak, at y567?2uC for non-activated



a TG; *b* DTA

3 Thermal analyses of non-activated and activated alunite ores

alunite, 522?1 and 502?2uC for 45 and 90 min activated alunite ores respectively, is 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 equation (2)[4,10,14]

$$KAl_3ðSO_4Þ_2ðOHÞ_6 ?KAlðSO_4Þ_2 zAl_2O_3 z3H_2O \quad (2)$$

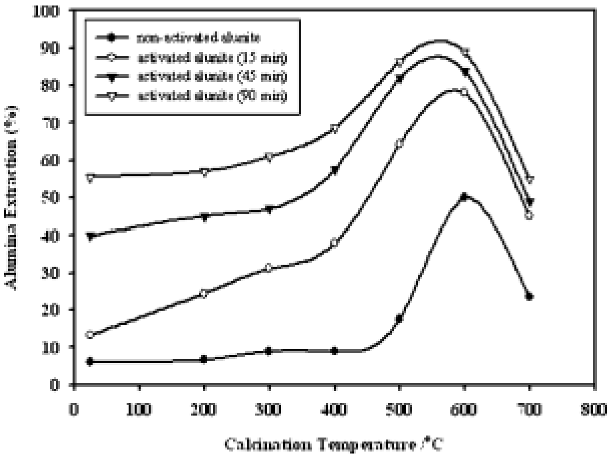
The exothermic peaks at y787uC for non-activated alunite ore appear immediately before the second endothermic peak at 822?1uC. This small exothermic peak was probably caused by the recrystallisation of $KAl(SO_4)_2$ into $K_3Al(SO_4)_3$ and $Al_2(SO_4)_3$,[4,10,14] as given in equation (3)

$$2KAl(SO_4)_2 ? \frac{2}{3}K_3Al(SO_4)_3 z \frac{2}{3}Al_2(SO_4)_3 \quad (3)$$

The second endothermic peak at 822?1uC for non-activated alunite ore is due to the desulphation,[4,10,14] 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 equations (4) and (5). The desulphation temperatures decreased to 797?2uC for 45 min activated alunite and to 772uC for 90 min activated alunite

$$\frac{2}{3}K_3Al(SO_4)_3 ? K_2SO_4 z \frac{1}{3}Al_2(SO_4)_3 \quad (4)$$

2 2



4 Effect of calcination temperature on alumina extraction from non-activated and activated alunite ores

steps of weight loss corresponding to the two endothermic peaks. The weight losses are y8% for the second endotherm (dehydration) and y22% as the total weight loss after the second endotherm (desulphation). This is an expected property for crystalline alunite. However, the mechanically activated alunite exhibited dehydration reaction starting from 100uC. This is a result of amorphisation and structural disordering, provided by mechanical activation.

Alumina extraction with/without calcination

The non-activated and mechanically activated alunite ores were calcined at 200, 300, 400, 500, 600 and 700uC respectively, for 60 min and leached in 1M H_2SO_4 solution for 30 min to investigate the effect of mechanical activation on alunite calcination temperatures (Fig. 4). The direct acidic leach results without calcination are also given in Fig. 4.

The possible chemical reaction occurring during extraction of alunite with sulphuric acid is as follows[6,9,15]

$$2KAl_3ðSO_4Þ_2ðOHÞ_6ðsÞ z6H_2SO_4ðaqÞ ?$$

$$2K^{z}_{ðaqÞ} z6Al^{3z}_{ðaqÞ} z10SO_4^{2\{}(aq) z12H_2O \quad (6)$$

The highest alumina extraction yields were obtained after calcination at 600uC for 1 h and leaching in 1M H_2SO_4 solution for 30 min at room temperature: 50% for non-activated alunite, 78% for 15 min activated alunite, 84% for 45 min activated alunite and 89% for 90 min activated alunite. Alunite is insoluble in water, acids or bases unless calcined. Alunite calcined at - 500uC dissolves owing to the decomposition of the structure. In spite of this fact, the mechanically activated alunite exhibited solubility in 1M H_2SO_4 solution without the calcination step. Alumina extraction values are 6% for non-activated alunite, 12% for 15 min activated alunite, 40% for 45 min activated alunite and 56% for 90 min activated alunite.

The dehydration of the alunite ore is completed in the 500–650uC temperature range for the non-activated alunite. Aluminium sulphate decomposes into alumina and sulphur trioxide at 750–850uC. However, at - 650uC, *c* alumina begins to change into *a* alumina.

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

The TG curve for non-activated alunite ore shows two

For this reason, the extraction yield increases up to 600°C and beyond this temperature, the yield decreases. Similar behaviours were also observed in previous studies.[3,6,9] As a result of amorphisation and structural disordering in alunite, alumina extractions have been obtained after the shorter calcination temperatures, followed by leaching mentioned in literature.[4,6]

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 500uC. On the contrary, the dehydration of mechanically activated alunite ore was started after 100uC. It is observed by X-ray diffraction analysis and thermal analysis that dehydration and desulphation temperatures of alunite ore decreased with mechanical activation, owing to amorphisation and structural disorders in alunite.

After calcination at 600uC for 1 h and leaching in 1M H_2SO_4 solution for 30 min, alumina extractions were 50% for non-activated alunite and 89% for 90 min activated alunite. In direct leaching of mechanically activated alunite without calcination step, alumina extraction values were obtained as 6% for non-activated alunite and 56% for 90 min activated alunite.

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