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# Extraction kinetics of alunite in sulfuric acid and hydrochloric acid

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**Abstract**

Extraction kinetics of alunite in sulfuric acid and hydrochloric acid were studied in a batch reactor. The effects of reaction temperature, acid concentration, particle size, calcination temperature, calcination time and $KF/Al_2O_3$ molar ratio on the extraction process were investigated. Experimental studies were carried out in the ranges of 35–95 °C for reaction temperature, 0.25–3.0 M for sulfuric acid, 0.5–0.6 M for hydrochloric acid, 76–182 μm for average particle size, 100–900 °C for calcination temperature, 15–60 min for calcination time and 0.15–0.90 for $KF/Al_2O_3$ molar ratio. The calcination temperature was the most important parameter affecting the extraction process followed by reaction temperature, particle size and acid concentration. Others had less effect. It was determined that the extraction process is controlled by diffusion through a product layer. The activation energies of the processes were found to be 19.1 and 18.5 kJ/mol for sulfuric acid and hydrochloric acid, respectively. The apparent rate constants were similar for both acids and found to be a function of acid concentration as $C^{0.33}$ and particle size $r^{-0.8}$.


*Keywords:* Alunite; Extraction kinetics; Sulfuric acid; Hydrochloric acid

## 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 $KAl_3(SO_4)_2(OH)_6$. It is colourless in the pure state, but is found in grey-white, yellow-white and reddish colours in nature due to impurities existing in structure. Alunite contains impurities such as silica, iron, titanium, magnesium and calcium; related to the occurrence in the reserves. In Turkey, alunite reserves are located in Şebinkarahisar-Giresun (15–20 million tons), Şaphane-Kütahya (7 million tons) and Foça-İzmir (5 million tons) regions (Anon, 2001). Its structure contains two components such as aluminium sulfate and potassium sulfate dissolved in water. However, natural alunite does not dissolve in water or acids. Alunite calcined at temperatures over

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500 °C dissolves due to the decomposition of the structure. It is widely used in the manufacturing of aluminium sulfate, potassium alum, alumina, potassium sulfate and sulfuric acid. Ore calcined at 600–650 °C is converted to the above mentioned products by acidic and basic extractions. Because of the increase of demand and the local scarcity of bauxite as the main source of alumina, a large number of studies have been made on the use of alunite as an alternative source of alumina (Sokal, 1945; Haff, 1946; Ting, 1952; Williams, 1979; Froisland et al., 1989; Şengil, 1991).

Alumina is produced from alunite by extraction with sulfuric acid according to the following method. First, alunite is calcined at about 900 °C. Thus, the aluminium sulfate in the structure is decomposed to sulfur trioxide and alumina. From the solid residue obtained after this calcination, potassium sulfate, the only soluble component may be extracted with hot water, and the insoluble residue containing alumina and silica remains. Aluminium sulfate is produced from the insoluble residue by extraction with sulfuric acid obtained through the process of calcination. Alumina is also produced by the calcination of aluminium sulfate (Sokal, 1945). In another, the alum is produced from ore calcined at 600–650 °C by extraction with sulfuric acid, and then, is calcined. This calcine is extracted with hot water to remove the soluble potassium sulfate. The remaining solid is obtained as alumina (Ting, 1952). In the last method, the potassium sulfate is extracted from the ore with hot and concentrated sulfuric acid. Acid-insoluble aluminium compounds are also extracted from the sulfation residue with hot water. Aluminium sulfate is precipitated from the water-extraction solution and calcined to alumina (Froisland et al., 1989).

Although these studies on the usage of alunite as an alternative source of alumina have been carried out, there does not exist any study on the extraction kinetics of alunite in acids in the literature. For that reason, the aim of this study was to investigate the extraction kinetics of alunite in sulfuric acid and hydrochloric acid, and to determine the effects of reaction temperature, acid concentration, particle size, calcination temperature, calcination time and KF/$Al_2O_3$ molar ratio. The extraction kinetics of alunite was investigated by using heterogeneous reaction models, and the best fitted equation to the experimental data was determined.

## 2. Materials and methods

The alunite used in the study was provided from Dostel Aluminum Sulphate Ltd. in Şaphane-Kütahya, Turkey. It was crushed, ground and sieved to give (−214+149), (−149+112), (−112+80) and (−80+71) μm size fractions using ASTM standard sieves. All the extraction experiments were carried out using −149 μm (−100 mesh) size ore except the study on the effect of particle size on aluminium extraction. The chemicals used in the extraction study and in the analysis were obtained from Merck Chemical.

The chemical analysis of the alunite was determined by the classical gravimetric method, in which silicates are melted with sodium carbonate. $K_2O$ was analysed by flame photometry. Its chemical composition is given in Table 1. Alunite was characterized by differential thermal analysis (DTA). DTA curve was recorded using Netsch 404 EP equipment with α-$Al_2O_3$ as a reference material, within the temperature range between the room temperature and 900 °C, and in air atmosphere at a heating rate of 10 °C/min.

A 5g sample was calcined at the working temperature for the desired time in Heraeus furnace, in air atmosphere at a heating rate of 10 °C/min. All test runs were done separately.

Extraction experiments were carried out in duplicate on the calcined sample using 100 mL acid solution in a batch heater-jacketed reactor of 150 mL capacity. The reactor content was stirred at 1250 rpm for 300 min and 1 mL samples of solution were taken at definite time intervals and filtered. The aluminium amount in the filtrate was determined by complexometry using EDTA solution, and hemotoxylin as indicator (Gülensoy, 1984).

The parameters used in the experiments were chosen as reaction temperature, acid concentration, particle size, calcination temperature, calcination time

Table 1
Chemical composition of alunite

| Component | $SiO_2$ | $Al_2O_3$ | $K_2O$ | $SO_3$ | $H_2O$ |
|---|---|---|---|---|---|
| %, w/w | 51.00 | 18.20 | 4.10 | 18.80 | 7.90 |