Amirkabir University of Technology
(Tehran Polytechnic)
Vol. 47, No.2, Fall 2015, pp. 1- 3

Amirkabir Journal of Science & Research -Civil & Environmental Engineering
(AJSR - CEE)

Modelling of Dehydroxylation and Desulphuration Kinetics of Haft Sandogh Alunite Ore

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(Received 23July 2010, Accepted 11 November 2015)

ABSTRACT

Solubility of alunite increases in acids and bases by calcinations. This process includes two main steps which are dehydroxylation and desulphuration. In this paper, after characterization of Haft Sandogh alunite ore, kinetics of dehyroxylation and desulphuration were studied. According to the results of thermogravimetric and weight loss, dehydroxylation of alunite occurs at 508 to 577˚C and desulphuration takes place at temperatures above 680˚C. It was observed that the dehydroxylation and desulphuration reaction rates increased with increasing temperature. Different kinetics models were used to evaluate kinetics data. By regression analysis and normalized standard deviation (NSD), the Avrami model was found to give the best fit to kinetic data. The reaction rate of both calcination processes were found to be less than one (i.e., n<1). This finding along with the high activation energy value (i.e., 117.4 kJ mol^{-1} for dehydroxylation and 215.4 kJ mol^{-1} for desulphuration) indicate that both reactions are controlled by chemical mechanism.

KEYWORDS

Alunite, Dehydroxylation, Desulphuration, Kinetics, Chemical control.

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1- INTRODUCTION

Alunite is one of the most important nonbauxite resource of alumina and potassium sulfate [1]. In metallurgy science, important alunite types are potassium alunite and natroalunite [2].

In Alunite structure, Aluminum and Potassium sulfates are insoluble in acids, bases or water. At temperatures higher than 600ºC, calcination in alunite causes a change in the structure that the solubility in any of the environments increases [3]. During the thermal decomposition of alunite, three processes occur that are respectively: dehydration, dehydroxylation and desulfurization.

A. Dehydration (around 220ºC)

$$KAl_3(SO_4)_2(OH)_6.xH_2O \rightarrow KAl_3(SO_4)_2(OH)_6+xH_2O \quad (1)$$

B. Dehydroxylation (511ºC to 586ºC)

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

C. Desulfurization (above 680ºC)

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

In this research, properties of Haft Sandogh Alunite ore was qualified then calcination kinetic and rate control steps were studied to determine disintegration reactions. Also the role of temperature and bed thickness in calcination was analyzed.

2- MATERIALS AND METHODS

Alunite ore was supplied from Haft Sandogh ore reserve located in Taykand, Qazvin, Iran. Chemical composition was determined using wet chemical analysis methods (gravimeter and flame-photometry) and containing minerals were defined using X-Ray diffraction method (XRD). Polished sections were prepared, in order to qualify the texture, size and shape of minerals involvement. Thermal behavior of the sample was investigated by Differential Thermal Analysis (DTA) and Thermos Gravimeter (TG).

The sample was crushed in three stages and finally the dimension was decreased by 75micrometers, by means of powder mills.

Crucible were weighted and then heated in a Muffle Furnace at a temperature of 105±5ºC in order to prevent the heat shock at the beginning of calcination process. Then they were immediately transferred to another Muffle Furnace with required temperature where calcination process occurs. Then crucibles were left in vacuum desiccator in order to be weighed after drying. Then the drop of the weights in each crucible was calculated. Three samples of 20 grams were put in Muffle Furnace (580ºC and 830ºC) for 24 hours in order to find the conversion ratio of dehydroxylation and desulfurization. The average drop was calculated to determine conversion rate of other drops at different temperatures and times.

3- DISCUSSION AND RESULTS

3-1- SAMPLE

Results showed that the sample contained 47.5% alunite, 46.71% quartz and about 5.71% kaolinite and major minerals proved by XRD method are quartz and alunite. Study of the polished sections with Scanning Electron Microscope (SEM) showed that alunite and quartz have a strong involvement.

DTA curve showed two great endothermic peaks and one small exothermic peak. The first endothermic peak in intense and sharp at 551.3ºC and the small exothermic peak can be caused by $\alpha-Al_2O_3$ or $\gamma-Al_2O_3$ phases or decomposition of potassium and aluminum sulfate to separate phases (the decomposition must be followed by heat absorption) [8]. The second exothermic peak takes place at 804.7ºC.

3-2- EFFECT OF ALUNITE CRUCIBLE BED THICKNESS ON CALCINATION

In order to analyze the effect of bed thickness of alunite crucible on calcination process, some experiments were conducted at 620 °C and 800 °C with different weights and bed thickness, but the identical crucible weight and volume.

3-3- EFFECT OF TEMPERATURE ON DEHYDROXYLATION AND DESULPHURIZATION

In order to study the effect of temperature on dehydroxylation, a series of experiments were conducted at 520°C, 550°C, 580°C, and 620°C. Also some tests were taken at 680°C, 730°C, 780°C, 830°C, and 880°C to explore the effect of temperature on desulfurization.

3-4- KINETIC INVESTIGATION OF DEHYDROXYLATION AND DESULPHURIZATION

To select the proper kinetic model for Alunite calcination, linearization analysis of kinetic parameters (shown in Fig. 1 and Fig. 2) was performed on the basis of fluid-solid kinetic equations of Avrami (4), Anti-Jander (3D) (5), Interface (6), Exponential (7), Prout-Tompkins (8) and Kroger & Ziegler (9) [5].

3-4-1- DEHYDROXYLATION KINETICS

To find the best-fit model for dihydroxylation process, different values was given to n in (4) and to evaluate the model, both linearization coefficient values (R^2) and Normalized Standard Deviation (NSD) were utilized [10].

Investigations represent that Avrami Kinetic Model with n=0.9 is the best-fit of dihydroxylation data.

3-4-2- DESLFURIZATION KINETICS

Results demonstrate that Avrami Equation gives the best result with n=0.75 resembling to laboratory data. For desulfurization as for the dihydroxylation, k' value was determined and activation energy was 215407.4 ($J.mol^{-1}$).

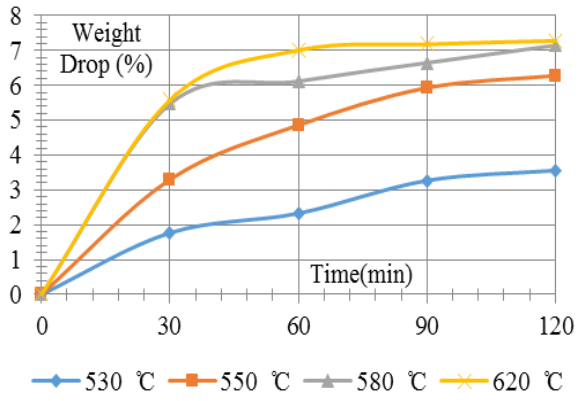

Fig. 1 Effect of temperature on dihydroxylation process

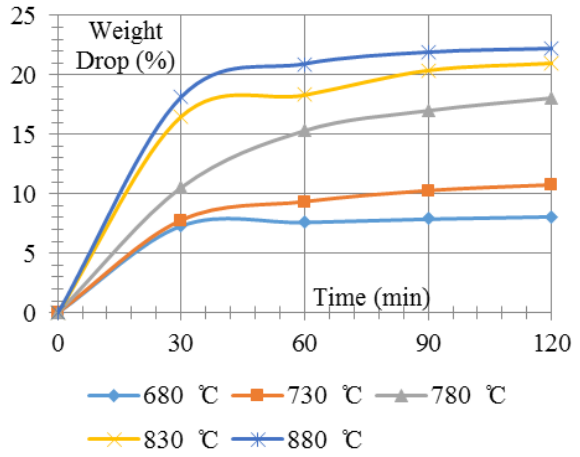

Fig. 2 Effect of temperature on desulfurization process

4- CONCLUSION

In this research, dihydroxylation and desulfurization kinetics of Haft Sandogh Alunite ore was investigated in Muffle Furnace. Results showed that when temperature rises, the rate of both processes increase. Previous studies represented that particle dimensions has no significant impact on the rate of dehydration. In this survey, bed thickness of crucible was found to have no effect on calcination process. Kinetic results of the experiments were analyzed, a diversity of kinetic models were evaluated and compared and the best-fit model to kinetic parameters was found to be the Avrami Model. Avrami Equation with n=0.9 for dehydroxylation and n=0.75 for desulfurization approved that both processes follow the chemical control mechanism. High values of activation energy resulted from Arrhenius Equation confirm the control chemical of both processes.

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