

# Investigation of Dissolution in Diammonium Hydrogen Phosphate Solutions of Gypsum

Turan Çalban, Nursel Keskin, Sabri Çolak, Soner Kuşlu

**Abstract**—Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is a mineral that is found in large quantities in the Turkey and in the World. In this study, the dissolution of this mineral in the diammonium hydrogen phosphate solutions has been studied. The dissolution and dissolution kinetics of gypsum in diammonium hydrogen phosphate solutions will be useful for evaluating of solid wastes containing gypsum. Parameters such as diammonium hydrogen phosphate concentration, temperature and stirring speed affecting on the dissolution rate of the gypsum in diammonium hydrogen phosphate solutions were investigated. In experimental studies have researched effectiveness of the selected parameters. The dissolution of gypsum were examined in two parts at low and high temperatures. The experimental results were successfully correlated by linear regression using Statistica program. Dissolution curves were evaluated shrinking core models for solid-fluid systems. The activation energy was found to be 34.58 kJ/mol and 44.45 kJ/mol for the low and the high temperatures. The dissolution of gypsum was controlled by chemical reaction both low temperatures and high temperatures.

**Keywords**—Diammonium hydrogen phosphate, Dissolution, Gypsum, Kinetics.

## I. INTRODUCTION

**G**YPSUM and anhydrite occur in arid and dry climatic conditions. It is located in layers. Gypsum layers take place as a result of evaporation of seas and lakes containing high salt. Gypsum is converted to anhydrite in more depth. Natural anhydrite is anhydrous calcium sulfate ( $\text{CaSO}_4$ ).

Precipitation of gypsum and anhydrite depends on the water temperature and salinity. Anhydrite occurs instead of gypsum under the conditions above these conditions. When anhydrite formation is continued, the precipitation of NaCl begins. Therefore, in many gypsum and anhydrite beds are found some rock salt and iron oxides [1], [2].

Raw gypsum attends paper and cotton textile materials as white paint and filler. It is used to increase the ash content of coal dusts in coal minings. Crude gypsum is used in increasing amounts every day in the cement industry. It facilitates the melting of nickel smelting and is used for fermentation in beer industry [1], [2]. Gypsum and anhydrite in Turkey are available in many areas [3].

T. Ç. is with Atatürk University, Engineering Faculty, Department of Chemical Engineering, Campus, Erzurum, TR 25240 Turkey (corresponding author to provide phone: 442-231-4578; fax: 442-231-4544; e-mail: turancalban@atauni.edu.tr).

N. K. was with Atatürk University, Erzurum, TR 25240 Turkey, She is now with the Project Unit Department of Technopolis, Atatürk University (e-mail: nkeskin@hotmail.com).

S. Ç. and S. K. are with the Chemical Engineering Department, Atatürk University, Erzurum, TR 25240, Turkey (e-mail: scolak@atauni.edu.tr, skuslu@atauni.edu.tr).

Studies done on the dissolution kinetics are summarized below. Reference [4] obtained boric acid and calcium phosphates from colemanite ore by using phosphoric acid. They determined the optimum conditions of dissolution. Reference [5] studied the dissolution of copper ore in aqueous  $\text{NH}_3\text{-(NH}_4)_2\text{SO}_4$  system. They searched the effects of ammonia concentration, ammonium sulphate concentration, the reaction time and the solid-to-liquid ratio. They leached 98.87% of copper in ore. Reference [6] researched the kinetics and mechanism of the dissolution of sphalerite in sodium nitrate solutions with sulphuric acid. According to selected kinetics model, the dissolution of sphalerite controlled by the diffusion film ash. The activation energy was found as 55 kJ/mol. Reference [7] made a study on the dissolution kinetics of bastnaesite in hydrochloric acid solutions. The parameters effected the dissolution were hydrochloric acid concentration, the temperature, the solid-to-liquid ratio and the particle size. The dissolution of bastnaesite controlled by the diffusion film ash, and the activation energy was 59.39 kJ/mol. Reference [8] investigated the dissolution kinetics of Chevreul's salt in hydrochloric acid solutions. The dissolution of Chevreul's salt controlled by the diffusion film ash, and the activation energy was 57 kJ/mol. Reference [9] researched the removal of calcium from waste-waters containing calcium chloride. They were reacting the distilled liquid waste with gaseous reagents. As a result, they precipitated as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) the calcium. The parameters such as gaseous velocities, the reaction time and the stirring speed were taken as factors affecting the precipitation efficiency. The precipitation yield was %44 under these conditions.

## II. EXPERIMENTAL PROCEDURE

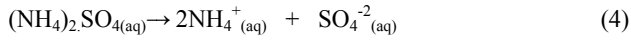
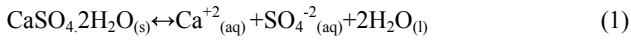
### A. Dissolution Tests

The dissolution experiments were performed in two different temperature groups. All of the experiments carried out in the ranges of the low temperatures and the high temperatures. First, the experiments were performed in the range of low temperatures. These temperatures was chosen as 25°C, 35°C, 45°C, 55°C. The total time of the experiments was taken as 150 minutes. Samples were taken at 30 min intervals. The water bath temperature was adjusted to 25°C. The prepared mixture was placed into the reactor, and stirring was performed by a magnetic stirrer. The stirring was initiated at 650 rpm value being a fixed speed. The stirring operation was continued throughout the reaction time. Withdrawing the sample from the solution every 30 minutes, the stirring was stopped. The sample was taken and filtered as 3 mL. After the samples are filtered, the amount of sulfate in solution were

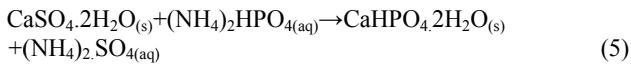
determined [10].

**B. Dissolution Reactions**

The reactions taking place in the solution can be written as:



When gypsum is added to the diammonium hydrogen phosphate solutions, the total reaction taking place in the solution can be written as:



The parameters and their values used in the experiments are given in Table I.

TABLE I  
PARAMETERS AND THEIR VALUES

Parameters	Levels of Parameters
Temperature (°C)	25 35 45 55 65 75 80 85 90
Reaction time (min.)	30 60 90 120 150
Solid/liquid ratio (g.mL <sup>-1</sup> )	1/100
Stirring speed (rpm)	650
Concentration (M)	0.5 1 2 3
Particle size (mm)	0.03482

\*While the effect of one parameter was studied, the values of the other parameters were kept constant.

**III. RESULTS AND DISCUSSION**

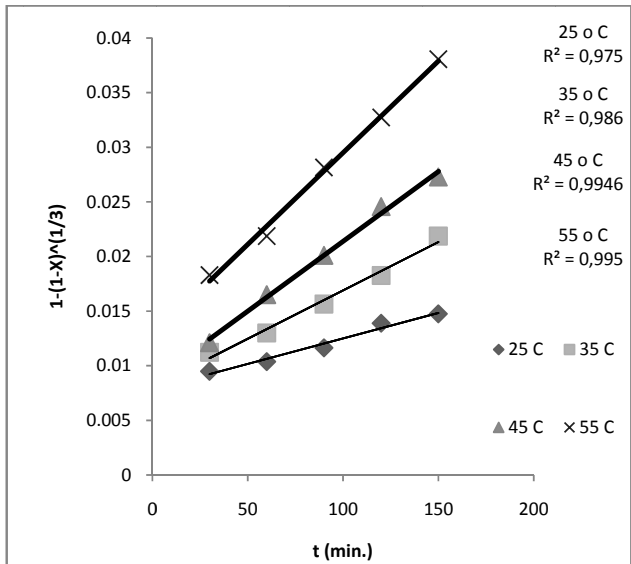


Fig. 1 Variation of  $1-(1-X)^{1/3}$  with time for the low temperatures (25-55°C)

In this study, pre-experiments were performed first. In light of these pre-experiments, the parameters affecting the dissolution kinetics of gypsum in diammonium hydrogen phosphate solutions were chosen as the temperature, the reaction time, the stirring rate and the solution concentration. According to the test results, graphs for 3 model were drawn and were calculated R2 values in relation to these models. It was found that the most appropriate model is the surface chemical reaction controlled model. This situation was shown in Fig. 1.

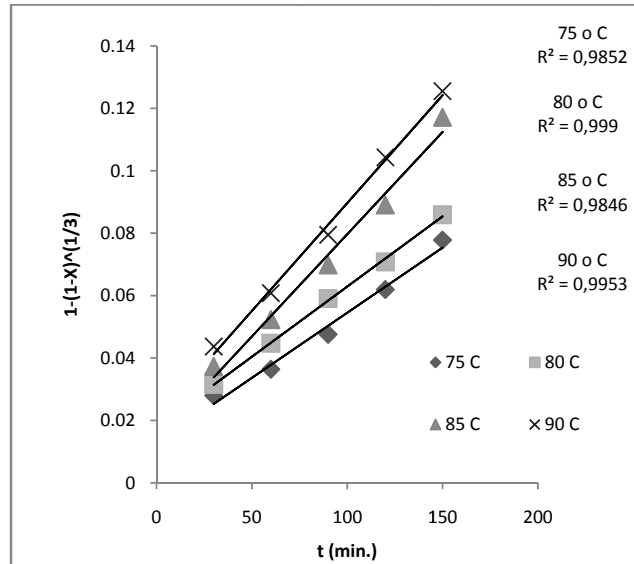


Fig. 2. Variation of  $1-(1-X)^{1/3}$  with time for the high temperatures (75-90°C)

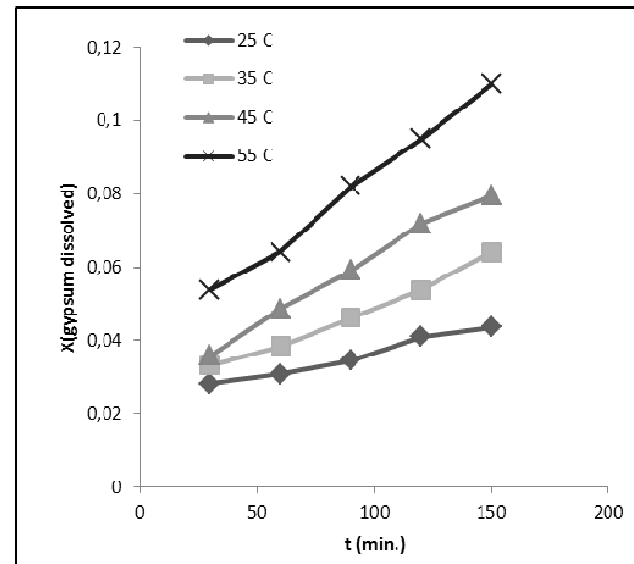


Fig. 3 Effect of the reaction temperature on the dissolution of gypsum

According to the test results, graphs for 3 models were drawn and were calculated R<sup>2</sup> values in relation to these models. It was found that the most appropriate model is the

surface chemical reaction controlled model. This situation was shown in Fig. 2.

The temperature is a factor of great importance for the leaching kinetics. The effect of reaction temperature was examined at 25, 35, 45, 55, 75, 80, 85, 90°C. The fact that the activation energies are different can probably be attributed to the differences of the chemical reaction mechanism. The effect of reaction temperature was investigated for the temperature range 25-55°C and 75-90°C temperatures. The dissolution curves obtained for 20-55°C are shown in Fig. 3 and 75-90°C are shown in Fig. 4. It can be shown from Figs. 3 and Fig. 4 that, the quantity of gypsum dissolved increases with increasing of reaction temperature.

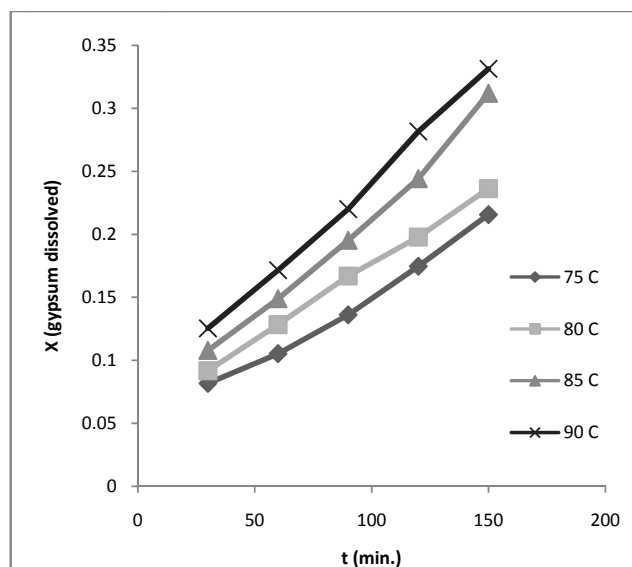


Fig. 4 Effect of the reaction temperature on the dissolution of gypsum

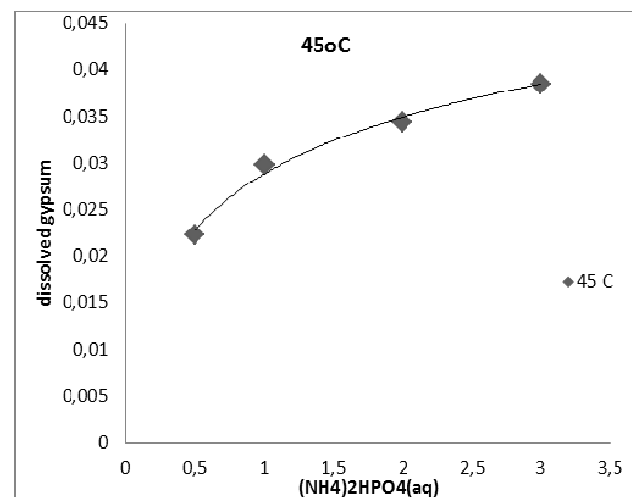


Fig. 5 Effect of the diammonium hydrogen phosphate concentration on the dissolution of gypsum at the low temperature

In general, the dissolution rate increases with increasing of concentration of reagent, but only up to a certain maximum

level. The effects of concentration of diammonium hydrogen phosphate solutions was studied by varying to 0.5, 1.0, 2.0 and 3.0 M. The dissolution curves are given in Figs. 5-6. It can be seen from the Figs. 5 and 6 that the dissolution level of the process increases with increasing in the concentration of diammonium hydrogen phosphate solutions.

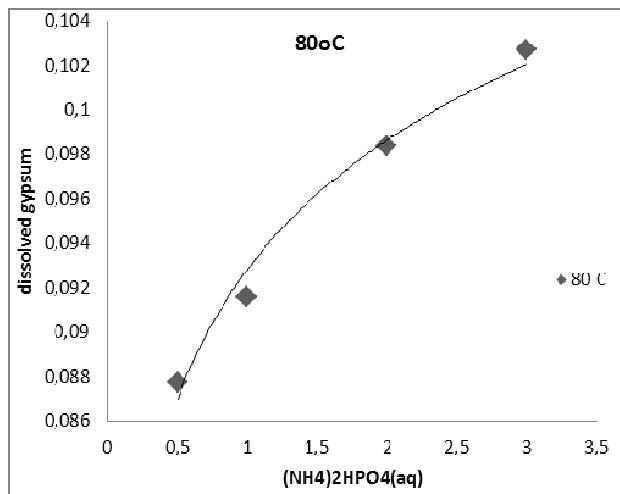


Fig. 6 Effect of the diammonium hydrogen phosphate concentration on the dissolution of gypsum at the high temperature

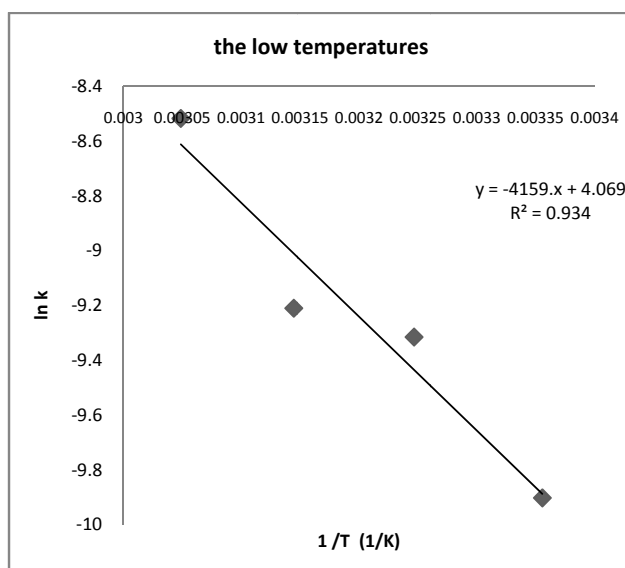


Fig. 7 Arrhenius plot of the dissolution process for the low temperatures

The Arrhenius plots of  $\ln k$  versus  $1/T$  were drawn for to found the activation energy of the reaction. Arrhenius plot of the dissolution process for reaction temperatures are shown in Figs. 7, 8. From the slopes of the straight lines of Figs. 7, 8, the activation energy of the reaction is found to be 34.58 kJ/mol and 44.45 kJ/mol. These values indicate the dissolution rate of gypsum is a chemical reaction controlled [8], [11]-[17].

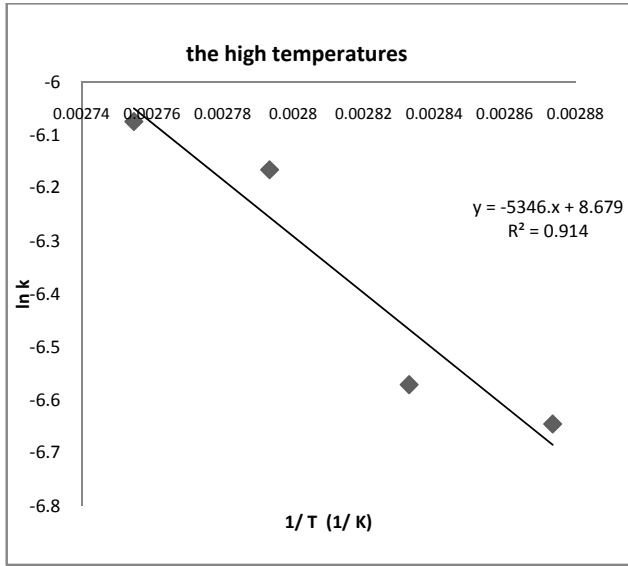


Fig. 8 Arrhenius plot of the dissolution process for the high temperatures

#### IV. CONCLUSIONS

The aim of the study was to investigate the dissolution kinetics of gypsum in diammonium hydrogen phosphate solutions in a mechanical agitation system. Based on the results obtained in this research, the following conclusions may be drawn:

The dissolution rate of gypsum increased with increasing in the low and the high reaction temperatures.

The dissolution rate of gypsum increased with increasing of diammonium hydrogen phosphate concentrations in the low and the high reaction temperatures.

The dissolution process follows a shrinking core model with the heterogeneous chemical reaction as the rate controlling step.

The activation energy of the reaction is found to be 34.58 kJ/mol and 44.45 kJ/mol for the low and the high temperatures.

Reaction rate expressions of dissolution of gypsum at the low temperatures and the high temperatures controlled by chemical reaction are as follows, respectively.

$$\left[1 - (1 - X_B)^{1/3}\right] = k_1 \cdot e^{-5159.5/T} \cdot t \quad (6)$$

$$\left[1 - (1 - X_B)^{1/3}\right] = k_2 \cdot e^{-5346.8/T} \cdot t \quad (7)$$

where  $k_1$  and  $k_2$  are constants depending on the diammonium hydrogen phosphate solution concentration, the solid/liquid ratio, the stirring speed and the particle size.

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