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DISSOLUTION OF MAGNESIUM FROM NATURAL MAGNESITE ORE BY NITRIC ACID LEACHING

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ABSTRACT : *Magnesite ($MgCO_3$) is a salt-type mineral and is found in large amounts in Turkey. In this study, dissolution of magnesite in nitric acid solutions was investigated. The effects of various parameters such as particle size, reaction temperature, solid to liquid ratio and acid concentration on the leaching process were examined. It was determined that the dissolution rate of magnesite increased with increasing reaction temperature and acid concentration, and decreasing solid to liquid ratio. No significant effect of particle size was observed on the dissolution of magnesium. The experimental data fitted the shrinking core model. The activation energy of the leaching process was calculated as 3.24 kJ/mol.*

KEYWORDS : *Magnesite; Nitric acid; Dissolution; Leaching; Kinetics.*

NİTRİK ASİT ÖZÜTLEMESİ İLE DOĞAL MANYEZİT CEVHERİNDEN MAGNEZYUMUN ÇÖZÜNMESİ

ÖZET : *Manyezit ($MgCO_3$) tuz tipi bir mineral olup Türkiye'de bol miktarda bulunur. Bu çalışmada manyezitin nitrik asit çözeltisi içindeki çözünürlüğü araştırılmıştır. Özütleme prosesi üzerine partikül boyutu, tepkime sıcaklığı, katı-sıvı oranı ve asit derişimi gibi parametrelerin etkileri incelenmiştir. Manyezit cevherinin çözünme hızının, tepkime sıcaklığı ve asit derişiminin artmasıyla ve katı-sıvı oranının azalmasıyla arttığı görülmüştür. Partikül boyutunun ise çözünme hızına önemli bir etkisi olmamıştır. Deneysel veriler kinetiğin, küçülen hacim modeline uyduğunu göstermiştir. Özütleme prosesinin aktivasyon enerjisi 3.24 kJ/mol olarak hesaplanmıştır.*

ANAHTAR KELİMELER : *Manyezit; Nitrik asit; Çözünme; Özütleme; Kinetik.*

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I. INTRODUCTION

Natural magnesite ($MgCO_3$) is one of the major sources of magnesium and its compounds. These products are widely used in the manufacture of refractories and metallurgical, chemical, ceramic and pharmaceutical industries. Natural magnesite contains theoretically 47.7% MgO and 52.3% CO_2. The magnesite reserves are abundant as a raw material source and available in Turkey. The large reserve in Turkey is about 160 million tones. The magnesite reserves are located in Kütahya-Eskişehir-Bursa and eastern region of Turkey [1].

Many researchers have been studied about dissolution of magnesite. Bayrak et al. [2] investigated the kinetics of the reaction between calcined magnesite and gluconic acid. They also investigated the effects of particle size, temperature, stirring speed, solid to liquid ratio and acid concentration on the leaching rate. They found that the dissolution was controlled by the surface chemical reaction. Fedorockava and Rashman [3] investigated the kinetics of the dissolution of MgO and the effects of concentration of H^+ ions, temperature and the type of the inorganic acid used (HCl, HNO_3 and H_2SO_4). Demir and Dönmez [4] studied the optimization of the dissolution of magnesite ore in citric acid solutions by Taguchi method. The optimum conditions for dissolution were found to be acid concentration of 2 M, reaction period of 120 min, temperature of 75°C, solid to liquid ratio of 0.125 g/mL and particle size of -319 µm. The extraction of magnesite was obtained as 99.9% under optimal conditions. Abalı et al. [5] investigated the dissolution of magnesite ore with H_2SO_4 solutions. The optimum conditions were found to be temperature of 65°C, solid to liquid ratio of 5 g/100 mL, acid concentration of 2 M, reaction period of 60 min and stirring speed of 300 rpm. Under these conditions the dissolution mass fraction of $MgCO_3$ was 96%. Laçin et al. [6] studied the dissolution kinetics of natural magnesite in acetic acid solutions. They reported that this process was controlled by chemical reaction. Özdemir et al. [7] investigated the magnesium recovery from magnesite tailings by HCl leaching and the production of magnesium chloride hexahydrate from leaching solution. They reported that the pseudo-second order reaction model was appropriate for the magnesium leaching. They produced $MgCl_2.6H_2O$ in a purity of 91% by evaporation of leaching solution. Although many researchers have been studied the dissolution of magnesite in various acidic media, there does not exist any study on the dissolution of natural magnesite by nitric acid solutions in the literature. Therefore, the aim of this study is to investigate the effects of particle size, reaction temperature, solid to liquid ratio and acid concentration on the dissolution of natural magnesite in nitric acid solutions. The dissolution kinetics was also investigated.

II. EXPERIMENTAL METHODS

The magnesite mineral used in this study was obtained from Eskişehir and Kütahya in Turkey. It was sieved using ASTM standard sieves, giving particle size fractions of -0.15+0.09, -0.25+0.15 and -0.85+0.25 mm. The original mineral sample was analyzed by using X-ray fluorescence analyzer and it was determined that the mineral contained 46.74% MgO, 1.89% CaO, 0.26% SiO_2, 0.07% Fe_2O_3, 0.01% Al_2O_3 and 51.03% loss on ignition. In addition, X-ray analysis showed that the main mineral is magnesium carbonate (Fig. 1). The chemicals used in the study and in the analyses were analytical grade Merck products.

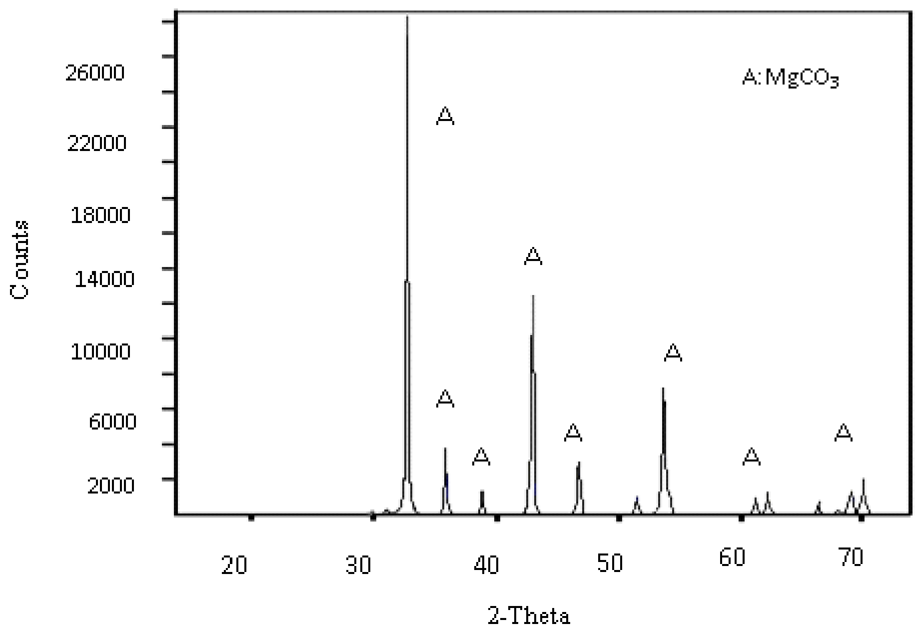

Figure 1. *X-ray diffractogram of the natural magnesite.*

In these leaching studies, the effects of particle size, reaction temperature, solid to liquid ratio and acid concentration were investigated. The ranges of these parameters are given in Table 1.

Table 1. *Parameters studied in the leaching experiments*

Parameters	**Values**			
Particle size (mm)	-0.15+0.09	-0.25+0.15	-0.85+0.25	
Temperature (^{o}C)	30	40	50	60
Solid to liquid ratio (g/L)	4	8	20	
Acid concentration (M)	1	2	3	

The leaching experiments were carried out in a 500 mL glass jacked-heated batch reactor equipped with a mechanical stirrer, a constant-temperature circulator to control the reaction temperature and a reflux condenser to avoid loss of solution by evaporation. In each experiment, 250 mL nitric acid solution at a certain concentration was put into reactor. After the desired reaction temperature was reached, a predetermined amount of the magnesite was added to the reactor while stirring the content of the reactor at a certain speed. From leaching solution, a definite amount of sample was taken at the predetermined time intervals and it was filtered immediately using a white filter paper. The amount of magnesium in the leach solution was analyzed volumetrically by EDTA method at pH 10 [8]. The amount of dissolved magnesium based on the amount of original magnesite ore was calculated. The data obtained were plotted as a function of dissolution fraction versus time.

III. RESULTS AND DISCUSSION

III. 1. Leaching reactions

When magnesium carbonate dissolves in nitric acid solution, the following reactions can be written:

$$2HNO_3(aq) \leftrightarrow 2H^+(aq) + 2NO_3^-(aq) \tag{1}$$

$$MgCO_3(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + CO_2(g) + H_2O(l) \tag{2}$$

The overall reaction can be written as follows:

$$MgCO_3(s) + 2HNO_3(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + CO_2(g) + H_2O(l) \tag{3}$$

The products of the reaction dissolve and become progressively smaller in size, and there is no solid product layer formed during the leaching reaction. These observations are in accordance with previous studies [5, 6].

III. 2. Effect of Particle Size

The effect of the particle size on the dissolution rate was investigated for three particle sizes (-0.15+0.09, -0.25+0.15 and -0.85+0.25 mm) in solutions containing 3M nitric acid at 60°C and 500 rpm. According to Figure 2, the particle size did not have a significant effect on the dissolution of magnesite. Similar results were found by Laçin et al. [6] and Özdemir et al. [7].

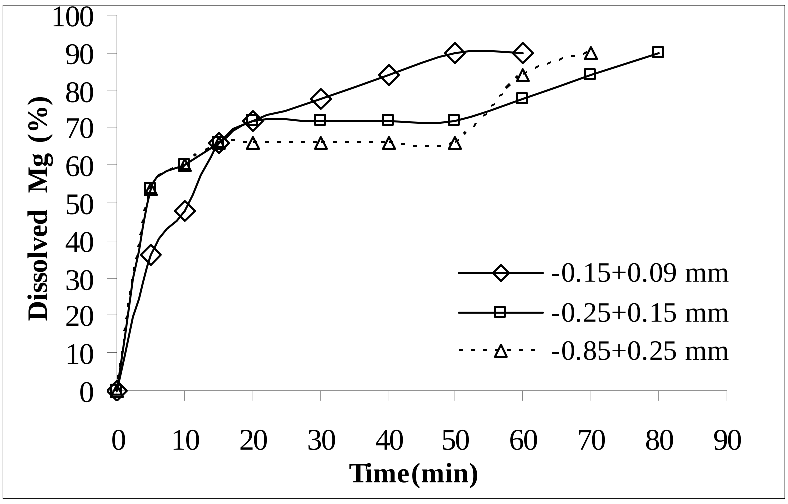

Figure 2. *Effect of particle size on the leaching of natural magnesite.*

III. 3. Effect of Reaction Temperature

The effect of the reaction temperature on the dissolution rate was studied in the range of 30-60°C under the conditions of 3 M nitric acid concentration, 500 rpm stirring speed and -0.15+0.09mm particle size. Figure 3 shows that the maximum magnesium recovery (90%) was obtained at 60°C in 50 min and it was observed that the dissolution rate increases as the reaction temperature increases due to the increase in the solubility of magnesite with temperature. This is in accordance with previous studies in literature in which it was reported that the reaction temperature had a noticeable effect on the dissolution of minerals [2, 3, 4, 6, 9].

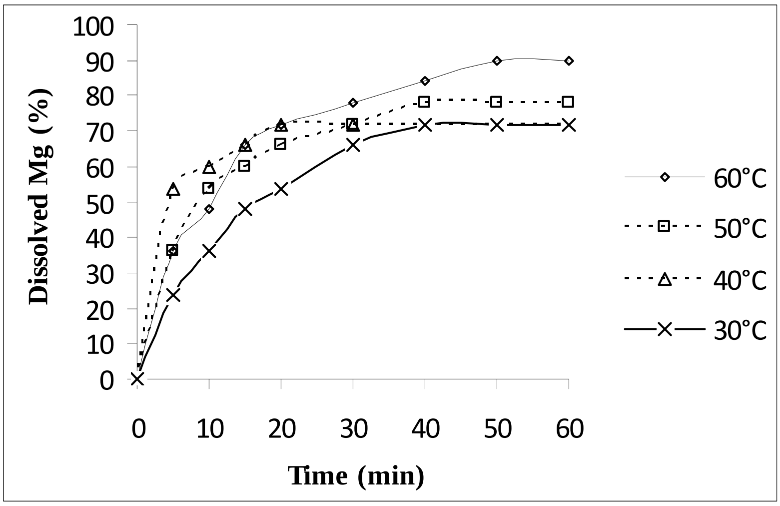

Figure 3. *Effect of reaction temperature on the leaching of natural magnesite.*

III. 4. Effect of Solid to Liquid Ratio

To determine the effect of the solid to liquid ratio on the dissolution rate, the experiments were performed at 4, 8 and 20 g/L under the conditions of 3 M nitric acid concentration, 500 rpm stirring speed, 60°C reaction temperature and -0.15+0.09 mm particle size. Figure 4 shows the results of the leaching experiments carried out with various solid to liquid ratios. According to the results, the leaching rate decreased as the solid to liquid ratio increased. This might be explained by the fact that the amount of reagent was not sufficient to leach magnesium from original magnesite ore when solid to liquid ratio was high. The same results were also found by Bayrak et al. [2] , Özdemir et al. [7] , Demirkıran [9] and Ekmekyapar et al. [10].

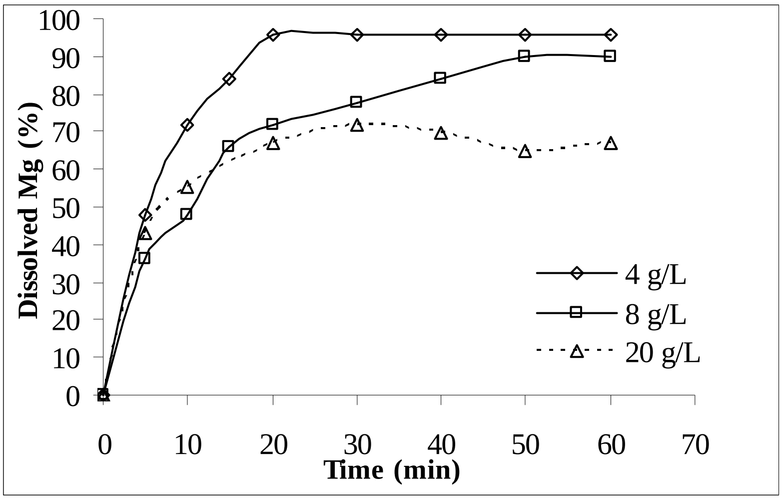

Figure 4. *Effect of solid to liquid ratio on the leaching of natural magnesite.*

III. 5. Effect of Acid Concentration

In order to determine the effect of the nitric acid concentration on the dissolution rate, the experiments were carried out in the concentrations of 1, 2 and 3 M while the temperature, particle size, stirring speed and solid to liquid ratio were kept constant at 60°C, -0.15+0.09 mm, 500 rpm and 8 g/L, respectively. The results in Figure 5 show the positive effect of the nitric acid concentration of 3 M on the dissolution of magnesium. The dissolution fraction values did not change for the acid concentrations of 1 M and 2 M in 60 min. Similar results were reported by Laçin et al. [6] They also reported that the amount of dissolved magnesium decreased when the acid concentration exceeded 3 M since the appearance rate of the product increased as the product approached to the saturation value on the surface of the solid particle and it forms a difficultly soluble solid film layer around the particle.

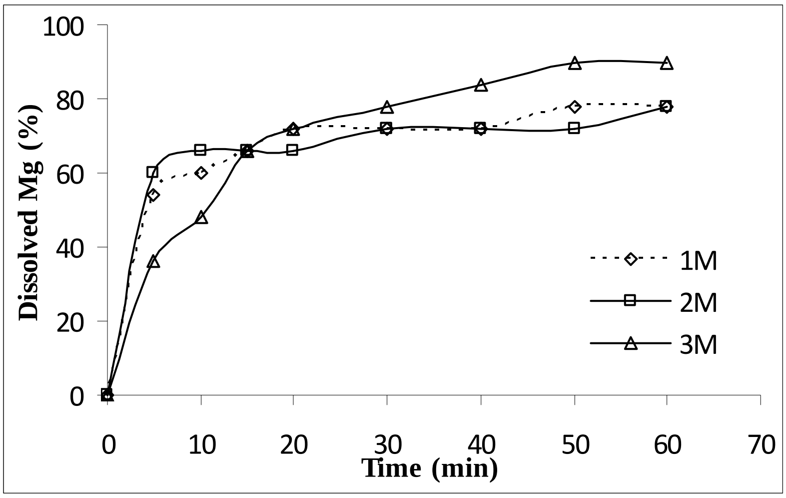

Figure 5. *Effect of acid concentration on the leaching of natural magnesite.*

III. 6. Kinetic Analysis

In order to investigate the kinetics of the leaching of magnesite by nitric acid solutions, the experimental data were analyzed by applying the shrinking core model for fluid-solid heterogeneous reaction systems. The reaction between a fluid and a solid may be represented by

$$A(fluid) + bB(solid) \rightarrow \mathrm{Pr}oducts \qquad (4)$$

According to the shrinking core model, the reacting particle shrinks during the reaction and finally it disappears if ash layer formation does not occur. In this case, the process consists of the following three steps [2, 10, 11, 12].

Diffusion of the fluid reactant from the fluid film surrounding the particle.

1. Reaction between the fluid reactant and the solid on the surface of the solid.
2. Diffusion of the reaction products from the surface of the solid through the fluid film back into the main body of fluid. Note that the ash layer is absent and does not contribute any resistance.

Noting from the stoichiometry of Eq. (4) that $dN_B = bdN_A$, we write

$$-\frac{1}{4\pi R^2}\frac{dN_B}{dt} = -\frac{b}{4\pi R^2}\frac{dN_A}{dt} = bk_s C_A \qquad (5)$$

If we let ρ_B be the molar density of B in the solid and *V* be the volume of a particle, the amount of B present in a particle is $N_B = \rho_B V$

$$-dN_B = -bdN_A = -\rho_B dV = -\rho_B d\left(\frac{4}{3}\pi R^3\right) = -4\pi\rho_B R^2 dR \quad (6)$$

$$-\frac{1}{4\pi R^2}4\pi R^2 \rho_B \frac{dR}{dt} = -\rho_B \frac{dR}{dt} = bk_s C_A \quad (7)$$

$$-\rho_B \int_{R_o}^{R} dR = bk_s \int_0^t C_A dt \quad (8)$$

The converted fraction of B solid is;

$$X_B = \frac{N_{Bo} - N_B}{N_{Bo}} = 1 - \frac{N_B}{N_{Bo}} = 1 - \frac{\rho_B\left(\frac{4}{3}\right)\pi R^3}{\rho_B\left(\frac{4}{3}\right)\pi R_o^3} = 1 - \left(\frac{R}{R_o}\right)^3 \quad (9)$$

$$\frac{R}{R_o} = (1 - X_B)^{1/3} \qquad C_A = C_{Ao}\left(1 - \frac{N_{Bo}}{bN_{Ao}} X_b\right) \quad (10)$$

$$dR = -\frac{R_o}{3}(1 - X_B)^{-2/3} dX_B \quad (11)$$

By combining Eqs. (8), (10) and (11)

$$\frac{dX_B}{(1 - X_B)^{2/3}\left(1 - \frac{N_{Bo}}{bN_{Ao}} X_b\right)} = \frac{3bk_s}{\rho_B R_o} C_{Ao} dt \quad (12)$$

where

$$A = \frac{N_{Bo}}{bN_{Ao}} \quad (13)$$

Consequently;

$$\int_0^{X_B} \frac{dX_B}{(1 - X_B)^{2/3}(1 - AX_B)} = \frac{3bk_s}{\rho_B R_o} C_{Ao} \int_0^t dt \quad (14)$$

The integration of the left-hand side of Eq. (14) is analytically difficult. Instead of this, it is more practical to use Matlab 2010 Package Program. The integrated form of Eq.(14) is

$$F(X) = kt \qquad (15)$$

The graphs of *F(X)* versus *t* are given in Figure 6 for the four reaction temperatures. The regression coefficient values R^2 were found in the range of 0.947 and 0.997. It indicates that the dissolution rate of the natural magnesite ore in nitric acid fit the shrinking core model.

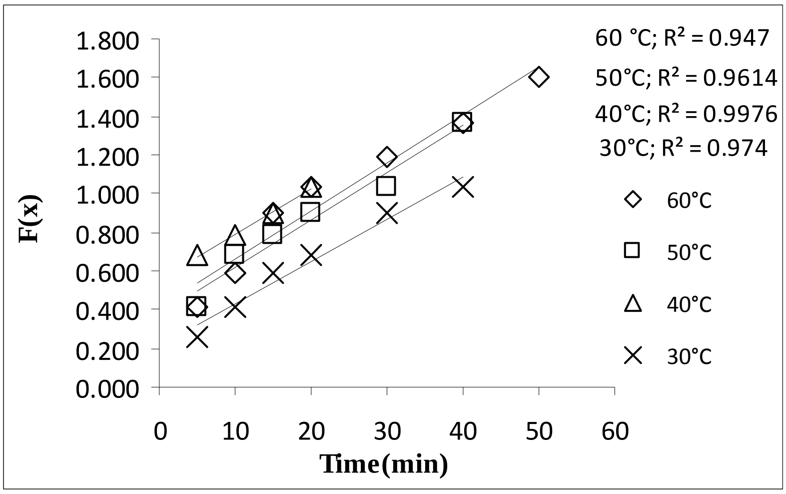

Figure 6. *The plot of F(X) vs. time for various reaction temperatures.*

The temperature dependence of the reaction rate constant can be expressed using the Arrhenius equation

$$k = k_o e^{-E_A/RT} \qquad (16)$$

where k_0 is the frequency factor, E_A the activation energy, *T* the temperature and *R* the gas constant. The Arrhenius plot of the process is shown in Figure 7. From the slope and intercept point of the straight line in Figure 7, the activation energy and frequency factor were calculated as 3.24 kJ/mol and 0.08 s^{-1}, respectively. The other researchers reported that the activation energy of the calcined magnesite in gluconic acid solution is 32.88 kJ/mol while that of the natural magnesite in acetic acid solution is 78.4 kJ/mol, that of the magnesite tailings in HCl solutions is 62.4 kJ/mol, that of the natural magnesite in HCl solutions is 48.33 kJ/mol and that of the aluminium from red mud in sulfuric acid is 7.39 kJ/mol[2, 5, 7, 13, 14].

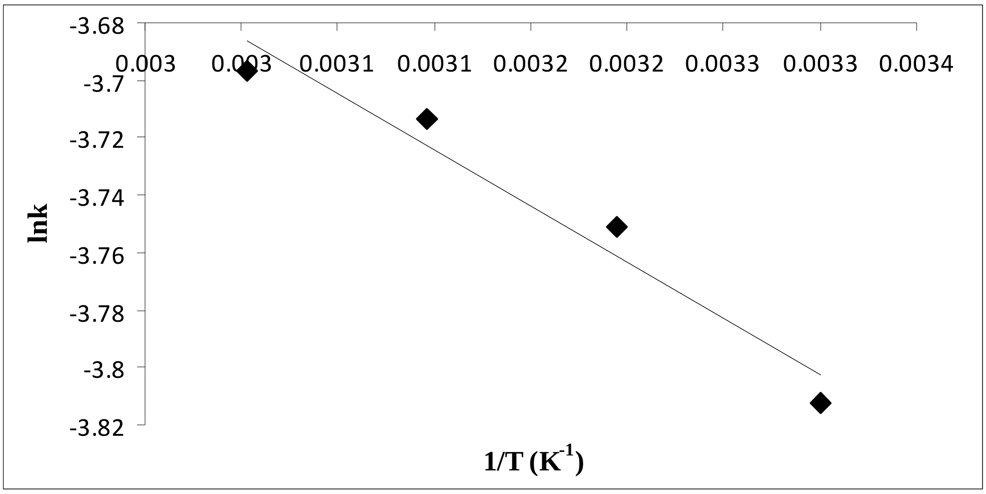

Figure 7. *Arrhenius plot for the leaching process.*

IV. CONCLUSIONS

The dissolution of natural magnesite in nitric acid solutions was investigated under the conditions of different particle size, reaction temperature, solid to liquid ratio and acid concentration. The main results of this work are as follows;

- The magnesium nitrate formed is used in the ceramic, printing, chemical and agricultural industries. Therefore, the usage of this process and determination of dissolution parameters are very important for industrial applications.
- The rate of transfer of magnesium to the solution increases with an increasing reaction temperature and acid concentration, and with decreasing solid to liquid ratio. The leaching process was not significantly affected by particle size.
- The dissolution kinetics follows a shrinking core model. The activation energy of the dissolution process was calculated to be 3.24 kJ/mol. The low activation energy is indicative of a process controlled by diffusion. Zhang and Muhammed [15] studied nitric acid leaching and they also determined that apatite dissolution is step-limited by diffusion.

V. ACKNOWLEDGEMENT

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VI. LIST OF SYMBOLS

b	stoichiometric coefficient
C_{Ao}	initial molar concentration (mol/L)
C_A	molar concentration (mol/L)
E_A	activation energy (kJ/mol)
k_s	rate constant for surface reaction (m/s)
k	reaction rate constant (s^{-1})
k_0	frequency factor (s^{-1})
N_A	moles of fluid reactant
N_{Ao}	initial moles of fluid reactant
N_B	moles of solid reactant
N_{Bo}	initial moles of fluid reactant
R	universal gas constant (J/mol K)
R	radius of unreacted core (m)
R_o	average radius of solid particle (m)
T	reaction time (min)
T	temperature (K)
V	reaction volume (cm^3)
X_B	fractional conversion
ρ_B	molar density of B in the solid (mol/cm^3)

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