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Investigation of dissolution kinetics of natural magnesite in gluconic acid solutions

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Abstract

In this study, the dissolution of magnesite particles in aqueous gluconic acid solutions was investigated in a batch reactor employing the parameters of stirring speed, particle size, temperature, solid/liquid ratio and acid concentration. The shrinking core model was evaluated for the rate increased by decreasing particle size and increasing the temperature and initially, the dissolution in terms of acid concentration and then fell with the increasing concentration. No important effect of stirring speed was observed and the dissolution rate decreased as solid/liquid ratio increased. It was shown that the model is:

$$-2.0\ \ln((1-X_{\mathrm{B}})^{1/3}+1.63)+1.0\ \ln((1-X_{\mathrm{B}})^{2/3}-1.63(1-X_{\mathrm{B}})^{1/3}+2.66)-3.47\arctan(0.58(1.23(1-X_{\mathrm{B}})^{1/3}-1))=\frac{3bk_{\mathrm{S}}C_{\mathrm{A0}}}{\rho_{\mathrm{B}}R}t$$

Dissolution curves were evaluated in order to test shrinking core models for fluid–solid systems. Consequently, it was determined that the dissolution rate is controlled by surface chemical reaction. The activation energy of the process was determined to be 61.7 kJ mol^{-1}.

Keywords: Magnesite; Gluconic acid; Chemical dissolution; Kinetics

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1. Introduction

Dissolution of the solid particles is a typical industrially relevant process, for instance in hydrometallurgy, medicine, oceanography, crystallography, ceramics and desalination as well as in a number of biological and environmental precipitation processes [1]. One of the solid particles is magnesite ore. Turkey has extensive magnesite ores. Magnesite (magnesium carbonate) is found in three main forms: (1) crude magnesite, primarily for use in chemicals, pharmaceutical industry as an anti-acid, agriculture, lime, in paper and sugar industries, (2) dead-burned magnesia, a durable refractory for use in cement, pharmaceutical industry, glass, steel and which is used in the metallurgical industries and (3) caustic calcined magnesia, for use in making oxychloride and oxysulfate cements and various environmental and chemical applications.

Several studies have been performed to determine the dissolution rate of magnesite. They found that the layer of the product film formed on the mineral surface affects the reaction rate and the level of this effect differs for every acid [2]. Raschman and Fedorockova [3] were researched the kinetics of the reaction between dead-burned magnesite and hydrochloric acid. They found that the dissolution of MgO is controlled by the chemical reaction of MgO with H^+ and apparent activation energy was 58–64 kJ mol^{-1} [3]. Dissolution kinetics of magnesite mineral in water with chlorine was investigated depend on temperature, solid/liquid ratio, stirring speed, particle size and gas flow rate [4]. Another chlorination study of magnesite was realized by Kennedy and Harris and the activation energy for this process was calculated as 80 kJ mol^{-1} [5]. Also, a kinetic study of the dissolution of magnesite in HCl and the kinetic analysis proved that the dissolution rate is controlled by the surface reaction [6]. Demir et al. were studied the leaching kinetics of magnesite in citric acid solutions and activation energy was obtained 61.35 kJ mol^{-1}. It was found that the dissolution rate was controlled by chemical reaction [7]. Similarly, the dissolution of magnesite in acetic acid being an organic acid was investigated by Laçin et al. Activation energy of leaching process was found

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Nomenclature

b	stoichiometric coefficient of solid B
C_{A}	concentration of acid reactant (mol L^{-1})
C_{A_0}	initial concentration of acid reactant (mol L^{-1})
E_{A}	activation energy (kJ mol^{-1})
k	reaction rate constant (s^{-1})
k_{S}	rate constant for surface reaction (m s^{-1})
k_0	frequency or pre-exponential factor (s^{-1})
N_{A}	moles of acid reactant
N_{B}	moles of solid reactant
N_{B_0}	initial moles of solid reactant
r_{C}	radius of unreacted core (m)
R	initial particle radius (m)
R_{g}	universal gas constant (J mol^{-1} K^{-1})
S	surface (m^2)
t	time (s)
T	temperature (K or °C)
V	reaction volume (L^{-1})
X_{B}	fraction of B converted, the conversion
X_{Mg}	fraction of Mg converted

Greek letter

ρ_{B}	molar density of solid reactant (mol L^{-1})

78.40 kJ mol^{-1}. It was determined that the reaction fits the chemical reaction controlled [8]. In the another study, the dissolution kinetics of calcite were researched in acetic acid solutions by Fred and Fogler and they found that dissolution is influenced by the transport of both reactants and products below pH 2.9 and pH values >3.7, the dissolution is controlled by the kinetics of surface reaction [9]. No study was found concerning the dissolution kinetics of magnesite in gluconic acid solutions.

Gluconic acid and gluconates having a great importance in manufacturing industries that are used in pharmaceutical, food, feed, detergent, textile, leather, photographic and concrete industries [10–12]. Gluconic acid and its salts can be produced by chemical, electrochemical, biochemical, bioelectrochemical methods [13–15]. Recently, one of the major method for producing gluconic acid and gluconates is fermentation [16]. Magnesium, calcium, sodium, zinc and manganese gluconate production by fermentation have been studied, by some researchers [17,18].

The dissolution kinetics of a solid compound depends on the processes taking place at the solid–liquid boundary; the processes are complex and involve both chemical reactions and mass transfer. The solid–liquid reactions can occur at the surface of the solid, in the film around the solid or in the liquid bulk phase. Different steps, such as mass transfer, chemical reaction and charge transfer, can determine the dissolution rate. The classical models used for solid–fluid reactions are the shrinking particle and shrinking core models. The shrinking core model has been suggested by many authors to be valid for leaching of magnesite [1].

Therefore, in this study, the dissolution kinetics of magnesite in aqueous gluconic acid solution was examined according to the modified shrinking core models, and the best fitted equation to the experimental data was determined. The effects of the particle size, acid concentration, reaction temperature, solid/liquid ratio and stirrer speed on the dissolution rate have been evaluated.

2. Materials and methods

The sample of magnesite ore used in experimental runs comes from a region of Refahiye, Erzincan, Turkey. A sample was completely soluble in HCl, its chemical composition was analyzed by the standard gravimetric and volumetric methods [19] and the chemical analysis results of the ore are given in Table 1. An X-ray diffraction pattern of the magnesite ore was obtained using a Rigaku 2000 JCPDS DMAX (29-1490) diffractometer (XRD) with Cu Kα radiation (30 kV and 30 mA and automatic monochromator) at a scanning rate 2θ of 2° min^{-1} (Fig. 1). In this figure, the XRD studies of the ore indicate $MgCO_3$ as the major compounds and $CaCO_3$, Fe_2O_3, SiO_2 as minor compounds.

After crushing and washing, the ore was ground and then sieved to different size fractions 1425, 725, 512, 338, 215, and 153 μm using ASTM standard sieves.

Gluconic acid used for leaching in these experiments was reagent grade (50 wt.% solution in water) Acros organics.

The dissolution process was carried out in a 500 mL cylinder glass batch reactor heated by a thermostat for keeping reactor contents at a constant temperature, equipped with a digital controlled mechanical stirrer, thermometer and a condenser to prevent losses by evaporation (Fig. 2). For each experiment, 250 mL volume of gluconic acid at a definite concentration was transferred into the reactor at the required temperature. The reaction was initiated by the addition of a small amount of magnesite, at time $t = 0$, while stirring the contents of the reactor at a certain speed.

From leaching solution, 2 mL sample were collected at the pre-determined time intervals and it was filtered immediately and the amount of magnesium in the leach solution was analyzed complexometrically by EDTA at the medium of buffer solution (about pH 10) [20]. For each experimental condition, the experiment was repeated twice, and the arithmetic average of the result of the two experiments was used in the kinetic analysis. The dissolution tests were performed as a function of several parameters, their range and values are given in Table 2.

Table 1
Chemical analysis of the magnesite

Component	Wt.%
MgO	47.3
CaO	0.43
Fe_2O_3	0.25
SiO_2	0.40
Loss on ignitation (at 850 °C)	51.62

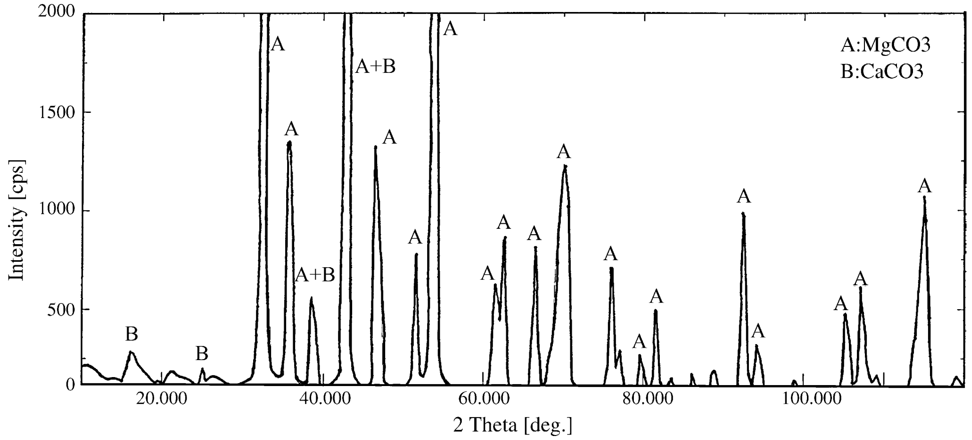

Fig. 1. The diffraction patterns of the magnesite ore.

3. Results and discussion

3.1. Dissolution reactions

Reactions between magnesite and gluconic acid can be written as follows:

$$2HC_6H_{11}O_{7(aq)} \leftrightarrow 2H_{(aq)}{}^{+} + 2C_6H_{11}O_{7(aq)}{}^{1-} \quad (1)$$

$$MgCO_{3(s)} + 2H_{(aq)}{}^{+} \rightarrow Mg_{(aq)}{}^{2+} + CO_{2(g)} + H_2O_{(l)} \quad (2)$$

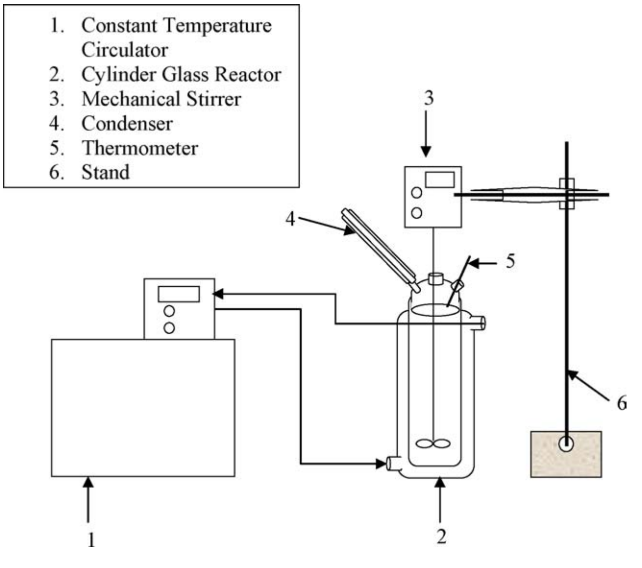

Fig. 2. Schematic view of experimental set up.

Table 2
The parameter values for dissolution of magnesite in gluconic acid solutions

Parameter	Value
Temperature (°C)	50, 55, 60[a], 65, 70
Acid concentration (mol L^{-1})	0.5, 1.0[a], 1.25, 2.0, 3.0
Particle size (μm)	1425, 725, 512, 338[a], 215, 153
Stirring speed (rpm)	500, 600[a], 700, 800
Solid/liquid ratio (g mL^{-1})	0.5/250, 1/250, 2/250[a], 4/250, 6/250

[a] The constant values used when the effect of other parameters was investigated.

$$MgCO_{3(s)} + 2HC_6H_{11}O_{7(aq)} \rightarrow Mg_{(aq)}{}^{2+} + 2C_6H_{11}O_{7(aq)}{}^{1-} + CO_{2(g)} + H_2O_{(l)} \quad (3)$$

3.2. The effects of parameters

3.2.1. Effect of particle size

The effect of a particle size on the dissolution rate was investigated for six different particle size in the range of 1425–153 μm. The others parameters was kept constant at the temperature of 60 °C, stirring speed 600 rpm, solid/liquid ratio 2/250 g mL^{-1} and concentration of gluconic acid 1.0 M.

According to Fig. 3, as the particle size decreases, the dissolution rate increases. This can be attributed to the increase of the contact surface. The results showed that the particle size had an effect on the dissolution of magnesite.

3.2.2. Effect of reaction temperature

Dissolution experiments of magnesite were carried out at the 50–70 °C temperature range in 1.0 M gluconic acid and 2/250 g mL^{-1} solid/liquid ratio at stirring speed of 600 rpm for 338 μm. Experimental results were shown in Fig. 4. From this figure, the dissolution rate increases clearly as the temperature

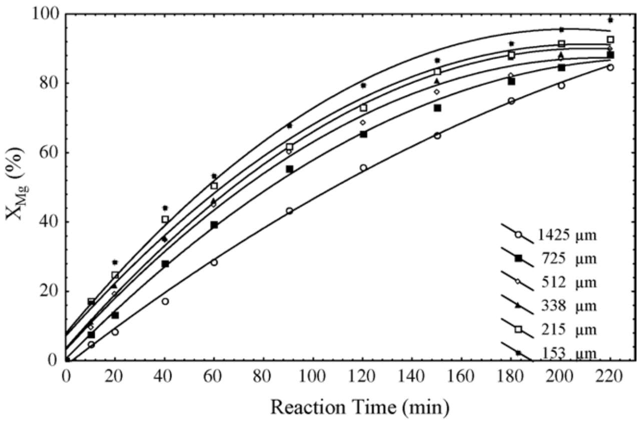

Fig. 3. Effect of particle size on the dissolution of magnesite (for 60 °C, 1 M, 2/250 g mL^{-1} and 600 rpm).

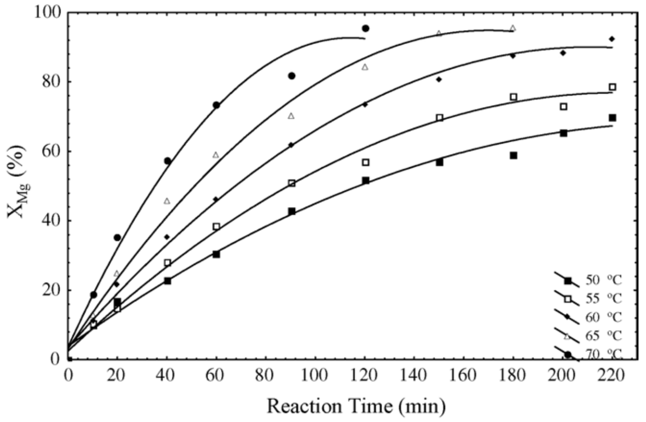

Fig. 4. Effect of temperature on the dissolution of magnesite (for 338 μm, 1 M, 2/250 g mL^{-1} and 600 rpm).

increases due to the exponential dependence of the rate constant in the Arrhenius equation.

3.2.3. *Effect of stirring speed*

To observe the effect of stirring speed on the dissolution rate, experiments were carried out using four different stirring speeds in the range of 500–800 rpm. As seen from the experimental results given in Fig. 5, the dissolution rate is practically independent of the stirring speed.

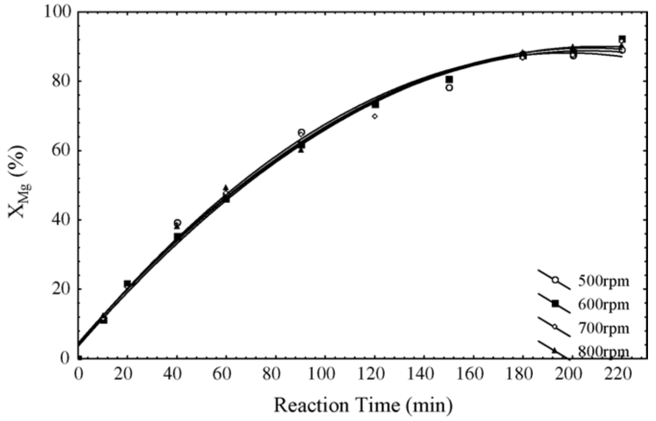

Fig. 5. Effect of stirring speed on the dissolution of magnesite (for 338 μm, 1 M, 2/250 g mL^{-1} and 60 °C).

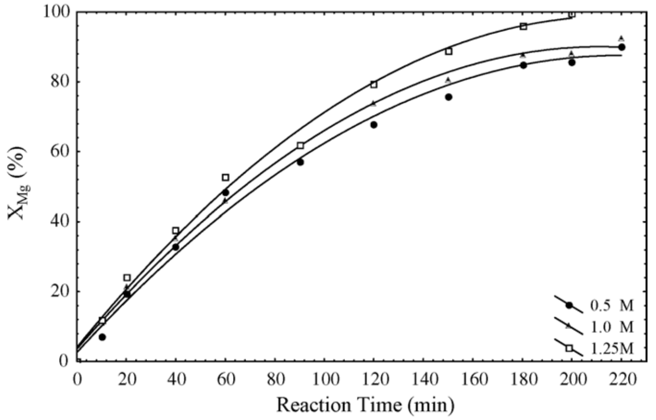

Fig. 6. Effect of acid concentration on the dissolution of magnesite (for 338 μm, 600 rpm, 2/250 g mL^{-1} and 60 °C).

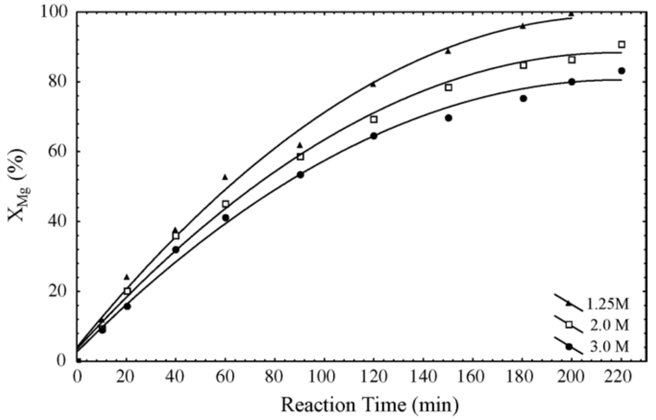

Fig. 7. Effect of acid concentration on the dissolution of magnesite (for 338 μm, 600 rpm, 2/250 g mL^{-1} and 60 °C).

3.2.4. *Effects of acid concentration*

In order to investigate the effect of the gluconic acid concentration on the dissolution rate, some experiments were performed with six different gluconic acid concentrations in the range of 0.5–3.0 M. The results of the experiments indicate that the dissolution rate increases by increasing the acid concentration until 1.25 M of gluconic acid concentration and more increase in the acid concentration caused decreasing rate as can be seen in Figs. 6–8. It could be attributed that the intensity of negative effect of water, the solvent, decrease after a certain value of acid concentration, was more dominant than that of positive effect of increase of acid concentration. Again, when the acid concentration exceeded a definite value, the number of hydrogen ions in the medium might decrease due to decrease of water amount more and more. In addition, this behaviour could be explained by the fact that as the acid concentration in the medium is increased, the appearance rate of the product increases and as the product reacted to the saturation value near the solid particle,

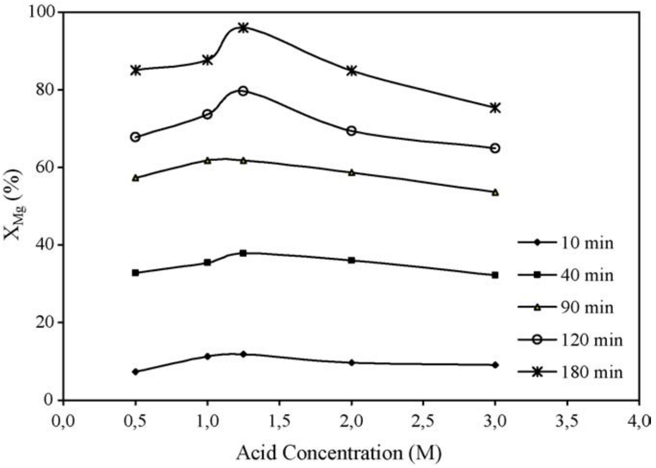

Fig. 8. Effect of acid concentration on the dissolution of magnesite for various times.

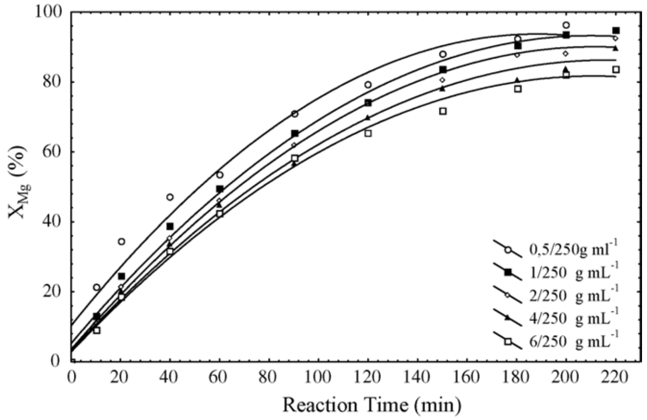

Fig. 9. Effect of solid/liquid ratio on the dissolution of magnesite (for 338 μm, 600 rpm, 1 M and 60 °C).

it forms a sparingly soluble product film layer around the particle. Consequently, the dissolution process slowed down after acid concentration of 1.25 M [21]. But, the leaching kinetics was basically investigated for the concentration range of 0.5–1.25 M. In addition, in the leaching experiments, the constant concentration value was selected as 1.0 M.

3.2.5. Effect of solid/liquid ratio

The effect of the solid/liquid ratio on the dissolution rate was studied in the range of 0.5/250–6/250 g mL^{-1} as shown in Fig. 9. According to Fig. 9, the dissolution rate decreased as the solid/liquid ratio increased. When solid/liquid ratio was increased, the amount of dissolved solid per unit liquid increase and hence the rate of dissolution decrease.

3.3. Kinetics analysis

The rate of reaction between a solid and a fluid can be expressed according to the heterogeneous reaction models. In the model, when ash is not formed the reacting particle will shrink during reaction and finally disappear. According to this model the following three steps are considered to occur in succession during reaction [22]:

1. diffusion of the fluid reactant from the main body of the fluid film to the surface of the solid,
2. reaction on the surface between the fluid reactant and the solid,
3. diffusion of the products in reaction from the surface of the solid through the fluid film back into the main body of the fluid. Note that the ash layer is absent and does not show any resistance.

According to the steps given above a heterogeneous reaction may be controlled by these steps. The fact that the dissolution rate was independent of the stirring speed indicates that the diffusion through the fluid film does not act as a rate-controlling step. So, the experimental data have been applied to the step 2 of shrinking core models. Shrinking core model is given as [22].

For the first order chemical reaction rate model:

$$-\frac{1}{S}\frac{\mathrm{d}N_{\mathrm{B}}}{\mathrm{d}t} = -\frac{b}{4\pi\, r_{\mathrm{C}}^{2}}\frac{\mathrm{d}N_{\mathrm{A}}}{\mathrm{d}t} = bk_{\mathrm{S}}C_{\mathrm{A}} \tag{4}$$

$$-\mathrm{d}N_{\mathrm{B}} = -b\,\mathrm{d}N_{\mathrm{A}} = -\rho_{\mathrm{B}}\,\mathrm{d}V = -4\pi\rho_{\mathrm{B}}r_{\mathrm{C}}^{2}\,\mathrm{d}r_{\mathrm{C}} \tag{5}$$

$$\frac{-1}{4\pi\, r_{\mathrm{C}}^{2}}\rho_{\mathrm{B}}4\pi\, r_{\mathrm{C}}^{2}\frac{\mathrm{d}r_{\mathrm{C}}}{\mathrm{d}t} = -\rho_{\mathrm{B}}\frac{\mathrm{d}r_{\mathrm{C}}}{\mathrm{d}t} = bk_{\mathrm{s}}C_{\mathrm{A}} \tag{6}$$

However the variation of C_{A} is too big to neglect during the reaction so, C_{A} cannot be accepted constant in Eq. (4) and this model is modified as follows [23]:

$$-\rho_{\mathrm{B}}\int_{R}^{r_{\mathrm{C}}}\mathrm{d}r_{\mathrm{c}} = bk_{\mathrm{S}}\int_{0}^{t}C_{\mathrm{A}}\,\mathrm{d}t \tag{7}$$

$$C_{\mathrm{A}} = C_{\mathrm{A}_0}\left(1-\frac{N_{\mathrm{B}_0}}{VbC_{\mathrm{A}_0}}X_{\mathrm{B}}\right),$$

$$M = \frac{N_{\mathrm{B}_0}}{VbC_{\mathrm{A}_0}} = \frac{0.024\,\mathrm{mol\ MgCO_3}}{0.25L\times 0.5\times 1.0M} = 0.19 \quad \text{and}$$

$$\frac{r_{\mathrm{C}}}{R} = (1-X_{\mathrm{B}})^{1/3} \tag{8}$$

consequently

$$\mathrm{d}r_{\mathrm{C}} = -\frac{R}{3}(1-X_{\mathrm{B}})^{-2/3}\,\mathrm{d}X_{\mathrm{B}} \tag{9}$$

By combining Eqs. (7)–(9):

$$\frac{(1-X_{\mathrm{B}})^{-2/3}\,\mathrm{d}X_{\mathrm{B}}}{(1-MX_{\mathrm{B}})} = \frac{3bk_{\mathrm{S}}C_{\mathrm{A}_0}}{\rho_{\mathrm{B}}R}\,\mathrm{d}t \tag{10}$$

where

$$\int_{0}^{X_{\mathrm{B}}}\frac{\mathrm{d}X_{\mathrm{B}}}{(1-X_{\mathrm{B}})^{2/3}(1-MX_{\mathrm{B}})} = \frac{3bk_{\mathrm{S}}C_{\mathrm{A}_0}}{\rho_{\mathrm{B}}R}\int_{0}^{t}\mathrm{d}t \tag{11}$$

It is too hard to solve Eq. (11) analytically so this equation was solved numerically with MATLAB 7.0 Package Program and the integrated rate expression is:

$$\begin{aligned}&-2.0\ln((1-X_{\mathrm{B}})^{1/3}+1.63)+1.0\ln((1-X_{\mathrm{B}})^{2/3}\\ &\quad -1.63(1-X_{\mathrm{B}})^{1/3}+2.66)\\ &\quad -3.47\arctan(0.58(1.23(1-X_{\mathrm{B}})^{1/3}-1)) = \underbrace{\frac{3bk_{\mathrm{S}}C_{\mathrm{A}_0}}{\rho_{\mathrm{B}}R}}_{k}t\end{aligned} \tag{12}$$

The plugging of all the experimental data into the integral rate was tested by multiple regression using Statistica Package 7.0 Program, and the multiple regression coefficients obtained for integral rate expression were calculated. In the calculations, it was seen that the very high value of regression coefficient correcting the rate expression was for surface reaction control (step 2). The coefficient value was calculated as 0.99. In order to confirm the results of these statistical analyses, the experimental data for each parameter were analysed by the graphical methods.

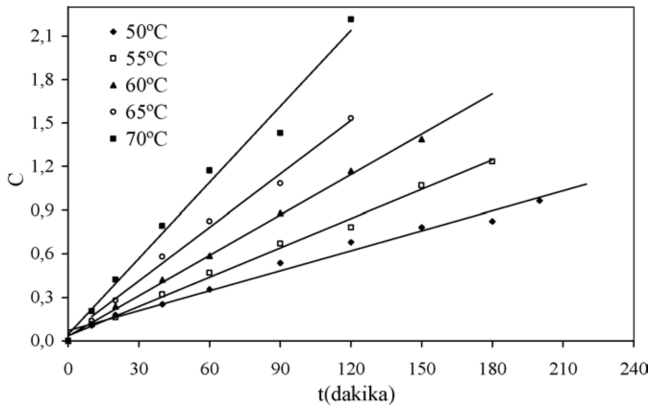

Fig. 10. C vs. t for various reaction temperatures.

If the left hand of Eq. (12) is called as C, the plot of C versus T is shown in Fig. 10 for the reaction temperatures (50–70 °C). The apparent rate constants were evaluated from the slopes of the straight lines.

From Arrhenius equation k term was known as

$$k = k_0 \mathrm{e}^{-E_{\mathrm{A}}/R_{\mathrm{g}}T} \tag{13}$$

As shown Fig. 11, the plot of $\ln k$ versus $\ln 1/T$ was obtained for the each value of the temperature and the following values are calculated:

$$E_{\mathrm{A}} = 61.7\,\mathrm{kJ\,mol}^{-1}, \qquad k_0 = 4.3 \times 10^7\,\mathrm{s}^{-1}$$

Thus, Eq. (12) could be given as

$$\begin{aligned} &-2.0\ln((1-X_{\mathrm{B}})^{1/3}+1.63)+1.0\ln((1-X_{\mathrm{B}})^{2/3} \\ &\quad -1.63(1-X_{\mathrm{B}})^{1/3}+2.66) \\ &\quad -3.47\arctan(0.58(1.23(1-X_{\mathrm{B}})^{1/3}-1)) \\ &\qquad = 4.3\times 10^7 \mathrm{e}^{-61.7/R_{\mathrm{g}}T}t \end{aligned} \tag{14}$$

The activation energy of a diffusion controlled process is characterized to be from 4.18 to 12.55 kJ/mol, while for a chemically controlled process; it is usually >41.84 kJ/mol [24].

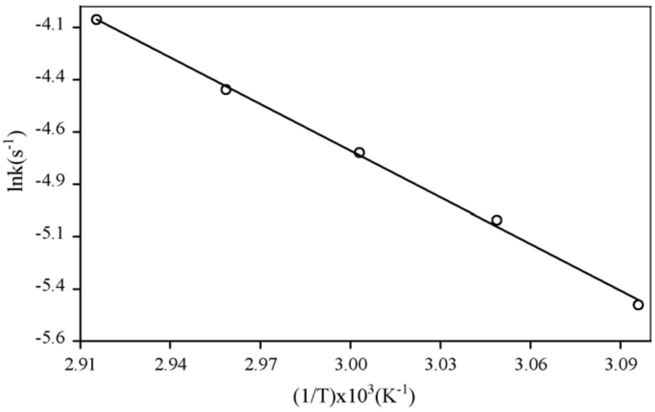

Fig. 11. Arrhenius plot for the dissolution of magnesite.

Such a value for the activation energy indicates that the leaching of magnesite with gluconic acid solutions is controlled by chemical reaction.

4. Conclusions

The dissolution kinetics of magnesite in gluconic acid solutions was studied. On the basis of the results of this study, the rate of dissolution of magnesite in gluconic acid was independent of stirring speed, which indicates that the reaction is not controlled by the diffusion in the liquid phase. The dissolution kinetics follow a shrinking core model with the surface chemical reaction as the rate-controlling step. The activation energy of the reaction was 61.7 kJ mol^{-1} and the reaction rate was very sensitive to the temperature in the range of 50–70 °C. Increasing the gluconic acid concentration increases the magnesite dissolution in the range of 0.5–1.25 M and decreases it in the range of 1.25–3.0 M. By the decreasing particle size of magnesite, the dissolution rate increases. The dissolution rate decreases as the solid/liquid ratio increases.

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