Dissolution Kinetics of Icel-Aydincik Dolomite in Hydrochloric Acid

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ABSTRACT

The dissolution of Icel-Aydincik dolomite in aqueous hydrochloric acid solution was investigated with respect to the effects of acid/dolomite mole ratio, solid/liquid ratio, particle size, stirring speed, time and temperature. It was observed that solubility of the dolomite ore increased with increasing acid/dolomite mole ratio, stirring speed, period of time, temperature, and with decreasing solid/liquid ratio and particle size. A kinetic model was applied to describe the dissolution and to analyse the kinetic data. By analysis of the experimental data, it was determined that the leaching process was controlled by the chemical surface reaction. The apparent activation energy of the leaching process was found to be 31.98 kJ mol^{-1}.

1. Introduction

Magnesite ($MgCO_3$) has been the most widely used magnesium resource due to its widespread occurrence and high magnesium content. For the past half-century, however, it has been dolomite [$CaMg(CO_3)_2$], which is of even wider occurrence than magnesite, that has dominated commercial extraction. In the production of primary magnesium and high grade magnesium oxide (MgO) from dolomite, dissolution is distinguished as the basic step. The kinetics and rate-limiting mechanism of dolomite dissolution have been less extensively studied than those of calcite dissolution. One of the studies of dolomite dissolution in hydrochloric acid (HCl) solution was carried out with the aid of a rotating disk system.[1] No rotational speed dependence was obtained for the dissolution rate, measured at 25 and 50 °C, so diffusion was not rate-limiting. The apparent activation energy for the reaction of 62 kJ mol^{-1} further supported the conclusion of surface reaction rate control.

An extensive set of experiments on dolomite dissolution was carried out[2] over a pH range of 0 to 10 and temperatures up to 65 °C. It was observed that heterogeneous chemical reactions were the rate-controlling mechanism below 35 °C. The authors used an impeller to stir the solution at 3000 rpm, and observed that stirring was not effective on the dissolution even at pH values from 3.0 to 4.4. Dissolution of the fresh dolomite surface was non-stoichiometric. It was determined that the Ca^{2+}/Mg^{2+} ratio released to the solution was greater than in the bulk solid. This effect of an apparently more rapid reaction with the $CaCO_3$ component of dolomite was very short-lived.[2]

Laboratory experiments on the dissolution kinetics of dolomites were conducted.[3] Emphasis was placed upon understanding how the effects of solvent motion and of carbonate lithology modify dissolution rates.

Dolomite dissolution rates in HCl as a function of pH and temperature were studied.[4] The experiments were conducted in aqueous HCl solutions over the bulk solution pH range of –0.39 to 4.44 and at temperatures of 25, 50 and 80 °C. Dissolution rates were dependent on the stirring speed at all temperatures and pH. The authors showed that dolomite dissolution rates at acid

conditions are proportional to a fractional power of $a_{H^+ surf}$, which is the aqueous H^+ activity at the mineral/solution interface.

A study was performed on the production of high purity magnesium oxide from magnesium chloride ($MgCl_2$) solutions obtained by leaching of Icel–Yavca dolomite in hydrochloric acid.[5] The dissolution of the $CaCO_3$ and $MgCO_3$ components was achieved with high extraction recoveries without making use of rotating action for the hydrodynamic conditions. Low activation energy (1.00 kJ mol^{-1}) was reached in the leaching experiments. The soluble ionic impurities, except for the calcium ions, were not at high levels in the chloride leach solutions, and the Ca^{2+} ions were precipitated by the carbonation process and then removed successfully.

The aim of this study was to investigate and discuss the dissolution parameters and dissolution kinetics of Icel-Aydincik dolomite ore in hydrochloric acid solution.

2. Experimental

2.1. Materials and Apparatus

Dolomite ore from the Aydincik area in the Icel province of Turkey was used. After being ground and dry sieved, parallel samples were prepared for chemical and mineralogical analysis. The chemical composition was determined by means of a Rigaku RIX 3000 X-ray spectrometer and Siemens SRS 3000 X-ray fluorescence spectrometer. The trace element content of the sample was determined with a Perkin Elmer 2380 atomic absorption spectrometer (AAS). The results of the chemical analysis, including the trace elements, are shown in Table 1.

Mineralogical analysis was performed by using a polarizing microscope with 160 times magnification of photographs of the thin sections prepared. Dolomite was the major mineral phase present. Limonite, quartz and clay-type minerals were minor mineral phases. The crushed and ground parallel samples were sieved with standard test sieves to obtain the desired particle size distributions for the dissolution experiments. Particle size distributions of the samples used in the experiments are shown in Table 2.

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Table 1 Chemical analysis of the dolomite ore.

Component:	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_3^{2-}	Li	B	Sr	Ti	SO_4^{2-}
(%)	30.79	21.29	0.02	0.02	0.04	47.61	<0.002	<0.002	0.01	<0.002	0.10

2.2. Procedure

The reaction between the dolomite ore and hydrochloric acid solution was performed in a 250 cm³ three-necked spherical Pyrex flask equipped with a thermometer, a mechanical stirrer and a reflux condenser.

A predetermined amount of ore of the required size was added into the hydrochloric acid solution of given concentration, solid/liquid ratio and at 20 °C or higher temperatures. After a specific time (2, 4, 6, 8, 10, 12 and 14 min), about 5 cm³ of hydrochloric acid solution at the same concentration as the solution at the beginning of each period was added. The higher temperatures of the leach solutions were achieved by means of a thermostatically-controlled water bath. Dissolution of the ore samples was performed under reaction conditions which were as follows: acid/dolomite mole ratio from 1.656 to 4.980, corresponding to the molarities of the acid from 3.00 to 9.02 mol dm⁻³ respectively, solid/liquid ratio from 15 to 55%, particle size from 75 to 2000 μm, stirring speed from 50 to 250 rpm and temperature from 20 to 80 °C.

The concentrations of Ca^{2+} and Mg^{2+} were determined by using an atomic absorption spectrophotometer (AAS). The solution was filtered after each dissolution experiment. The loss in mass of the solid phase after leaching was calculated from the difference between the mass of solids before and after the dissolution. Finally the undissolved solid residue was analysed by X-ray fluorescence (XRF) spectrometry.

3. Results and Discussion

3.1. Effect of Acid/Dolomite Mole Ratio

The effects of acid/dolomite mole ratio on the dissolution of calcium and magnesium were investigated at 20 °C on the sample sized ~2.000 mm. The dissolution tests were carried out at 25% solid/liquid ratio at the initial acid/dolomite ratios of 1.656, 2.484, 3.313, 4.151 and 4.980, depending on the acid strength, for 14 min. The stirring speed was chosen as 100 rpm. The extraction recoveries of calcium and magnesium versus

Table 2 Effect of particle size on dissolution of the dolomite ore (acid/dolomite mole ratio: 3.313; solid/liquid ratio: 25%; stirring speed: 100 rpm; temperature: 20 °C; dissolution period: 14 min).

Particle size/mm	Mass/%	Mg^{2+} recovery/%	Ca^{2+} recovery/%
~2.000 –1.000	0.76	70.60	74.00
~1.000 –0.500	31.22	75.65	78.00
~0.500 –0.250	42.13	91.85	91.88
~0.250 –0.106	22.84	98.60	98.65
~0.160 –0.075	1.78	100	100
~0.075	1.27	100	100

different acid/dolomite mole ratios are shown in Fig. 1.

It is obvious that the mole ratio of the acid has a significant effect on the dissolution of the dolomite. After the 14 min period, 76.00% of Ca^{2+} and 74.40% of Mg^{2+} were dissolved at an acid/dolomite mole ratio of 3.313. As the ratio was increased the recoveries increased, but they did not change much at the higher ratios. A significant point observed was that at low acid/dolomite mole ratios the dissolution rates of Ca^{2+} ions were higher than those of Mg^{2+} ions during the leaching. It is speculated that in the extraction process, oxygens in the Ca-O and Mg-O bonds of the solid particles are exchanged by oxygens from water of hydration. Moreover, H^+ ions from the acid adsorbed on to the particle surfaces cause hydrated surface formations which are responsible for the detachment process. The rate of dissolution is possibly dependent on the degree of hydration. This is consistent with the results obtained by earlier researchers.[1–6]

3.2. Effect of Solid/Liquid Ratio

Within this series of tests, the initial acid/dolomite mole ratio and the dissolution temperature were kept constant at 3.313 and 20 °C respectively. The amounts of solids were changed to obtain the desired ratio since the liquid volume was kept constant. The stirring speed was adjusted to 100 rpm and the time period was chosen as 14 min.
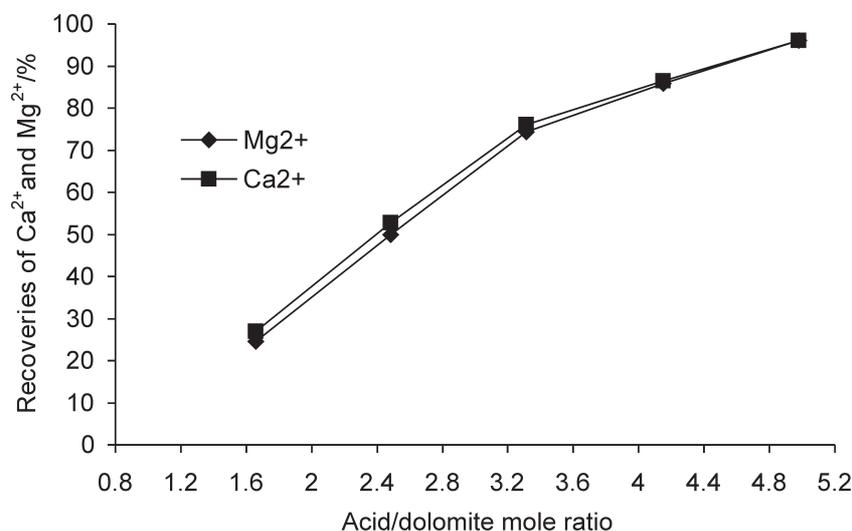
Figure 1 Effect of the acid-to-dolomite mole ratio on the extraction recoveries of Ca^{2+} and Mg^{2+} from the dolomite ore.
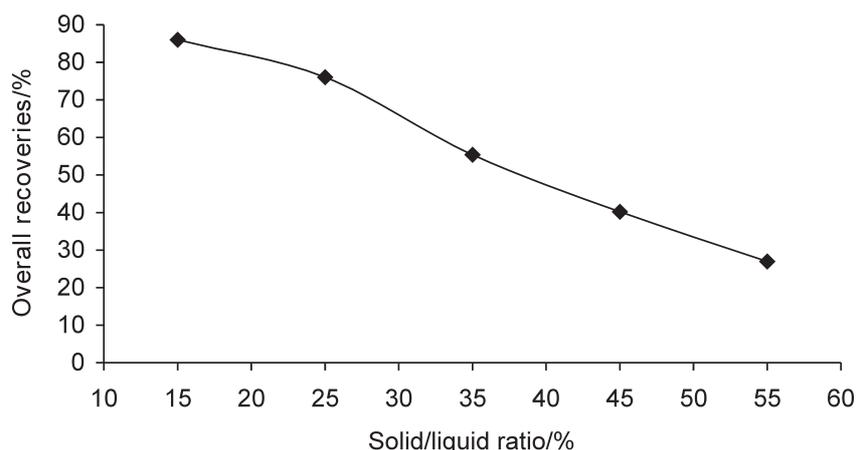
Figure 2 Effect of the solid/liquid ratio (m/v) on dissolution recoveries of the dolomite ore based on the mass losses.

The results presented in Fig. 2 suggest that the overall dissolution recoveries substantially decrease with an increase in the amount of solid consuming the acid in the solution. However, changes in the recoveries were not significant when the ratio was less than 25.00%. This result is probably related to the acid/dolomite mole ratio, since the amount of the solid increases and the dissolved amount decreases with the same amount of acid in the leaching.

3.3. Effect of Particle Size

It is shown in Table 2 that dissolution recoveries of the Mg^{2+} and Ca^{2+} ions increased as the particle size decreased. This behaviour can be explained by the increase in the specific surface area of the solid particles in contact with the acid solution. The smaller the particle size, the greater are the surface and interfacial areas between the solid and liquid, and therefore, the higher is the rate of dissolution of the sample; further, the smaller is the distance that the solute must diffuse within the solid, as already indicated.

3.4. Effect of Stirring Speed

For laminar flow, the rate of mass transfer (J) is given by Eq. (1),[7] where Sc is the Schmidt number, v is the kinematic velocity, w is the stirring speed, C_o is the bulk acid concentration, and C_1 is the acid concentration at the solid/liquid interface.

$$J = [(0.62048Sc^{-2/3}) (vw^{1/2}) (C_o - C_1)] / (1+0.2980Sc^{-1/3} + 0.1451Sc^{-1/2}) \quad (1)$$

In order to determine the effect of stirring speed on the dissolution recovery, tests were conducted by varying the stirring speeds from 50 to 250 rpm for different ambient temperatures. In each test, the mole ratio, solid/liquid ratio and dissolution period were kept constant as 3.313, 25% and 6 min, respectively. The recoveries calculated are based on the mass loss and correspond to the overall dissolution.

The overall dissolution recoveries are plotted as a function of $w^{1/2}$ in Fig. 3. The curves show that the dependence on stirring speed indicates some transport limitation on dissolution recoveries. The data suggest that at 20 °C dissolution does not depend on the stirring speed. However, the runs at 35, 50, 65 and 80 °C do show variation with the speed, indicating some transport limitation on the dissolution rates.

3.5. Effect of Elapsed Time and Dissolution Temperature

Experiments were carried out at the dissolution temperatures chosen for the periods of 2–14 min by using the acid/dolomite mole ratio 3.313 and a solid/liquid ratio of 25%. The stirring
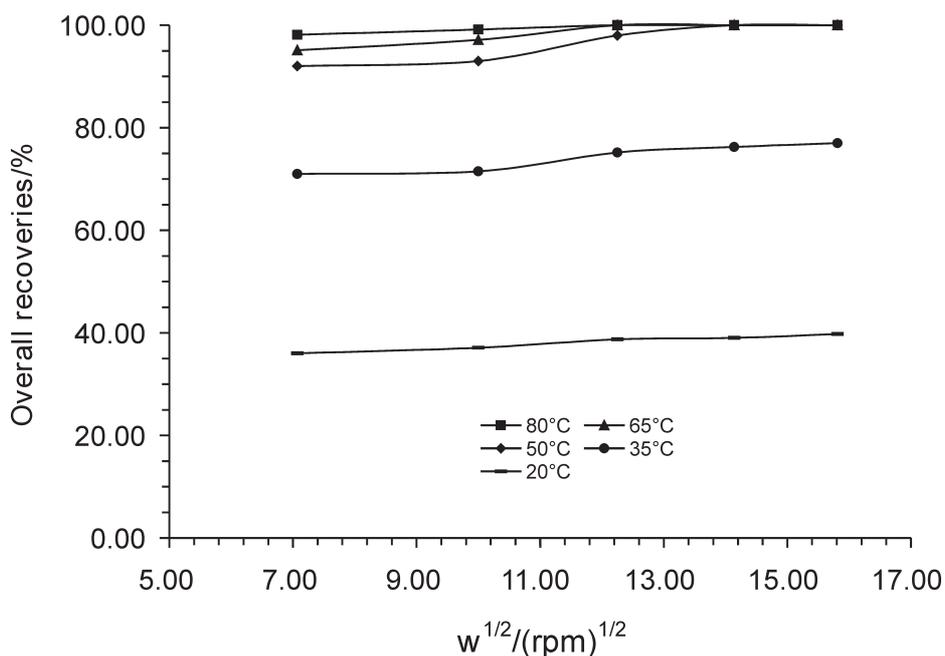

Figure 3 Dependence of the overall dissolution recoveries on the square root of the stirring speed at different temperatures.
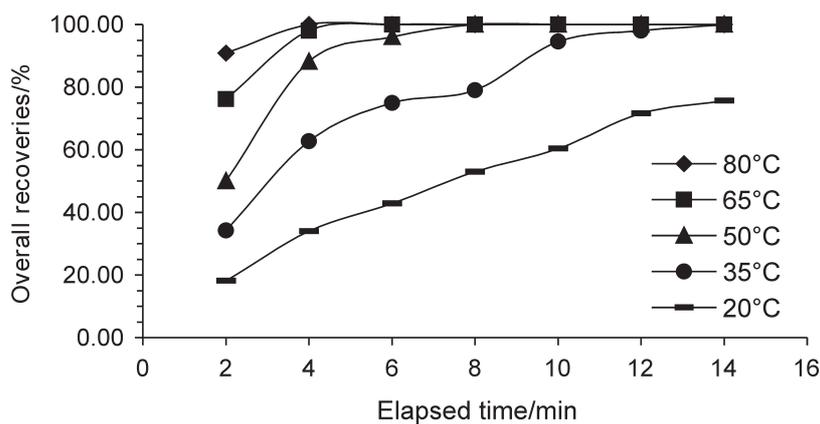
Figure 4 Dependence of dissolution recovery on the elapsed time at various temperatures.
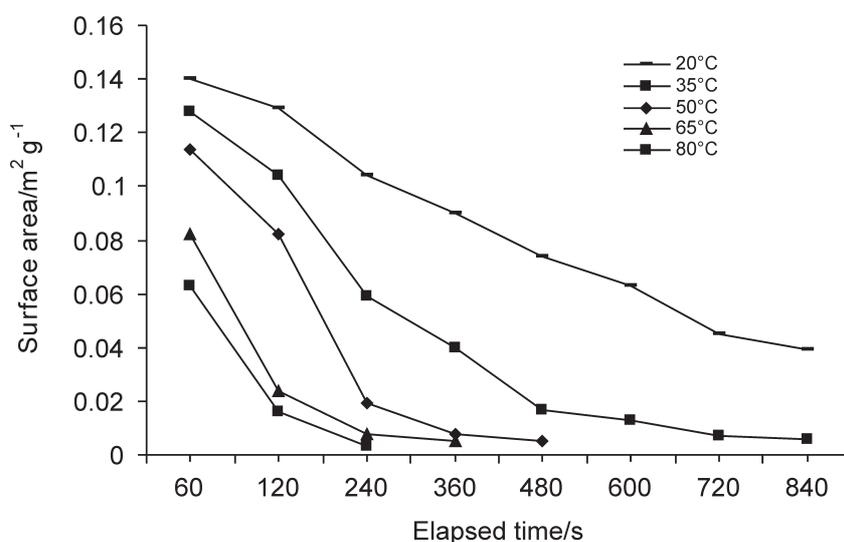

Figure 5 Final specific surface areas of the samples undissolved as a function of time at various temperatures.

speed was kept constant in all the experiments at 100 rpm. The recoveries are plotted against the time periods for the temperatures 20–80 °C and are shown in Fig. 4. It is seen that at constant hydrodynamic conditions, as the elapsed period increases the dissolution recovery increases for all the temperatures, but under these conditions, at low temperatures, the reaction takes longer periods. Higher dissolution recoveries were achieved at 65 and 80 °C within comparatively shorter periods. This means that the rate of dissolution increases with increase in temperature. As a result, a low residence time can be achieved as the reaction temperature increases.

3.6. Dissolution Rates

In order to calculate the dissolution rates, the derivative of the concentration-time plot is necessary. One mole of Ca^{2+} and one mole of Mg^{2+} that enter the solution correspond to one mole of dolomite that dissolves. The rate of dissolution (r) can be obtained by measuring the concentrations (dc) over the elapsed time (dt) and multiplying by the ratio of (V/S). It is described by Eq. (2),[8] where dc corresponds to the molar concentration of the dolomite dissolved (mol cm^{-3}), dt designates the leaching period (h), V represents the volume of the leach solution (65 cm^3 in all the experiments) and S refers to the specific surface area of the undissolved particulate sample, which was obtained at the end of each run (m^2 g^{-1}).

$$r = (dc/dt)(V/S) \qquad (2)$$

As shown in Table 3 the dissolution rates begin increasing from the initial value immediately after the start of a run for all the temperatures. Non-linear curves were obtained at all the bulk temperatures. The solubility of the dolomite sample in leaching increases with temperature to give a higher rate of extraction. Further, the diffusion conditions at the surface of the particles in the solution increased with rise in the temperature and this improved the rate. At 20 and 35 °C, gradually increasing rates were observed and the overall dissolution took about 14 min. However, at 50, 65 and 80 °C the rate increased sharply and the total dissolution took shorter periods. At higher reaction temperatures faster dissolutions were achieved.

Table 3 Dissolution rates of the dolomite sample at various temperatures as a function of time (acid/dolomite mole ratio: 3.313; solid/liquid ratio: 25%; particle size: ~1.000 mm; stirring speed: 100 rpm).

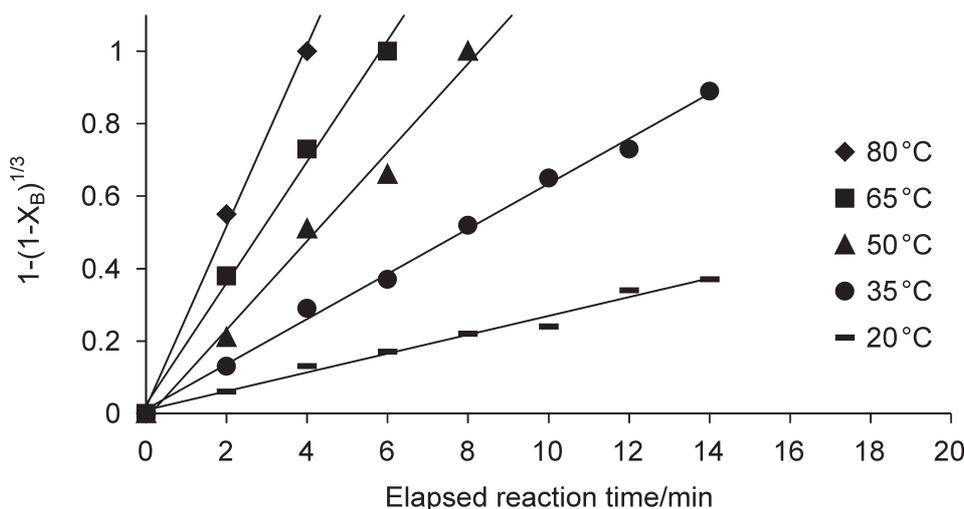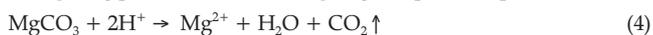| Elapsed time/s	Dissolution rate/10^{-3} g mol m^{-2} s^{-1}				
	20 °C	35 °C	50 °C	65 °C	80 °C
60	1.42	2.73	4.39	10.57	17.19
120	1.23	2.98	5.28	31.94	51.10
240	1.48	4.78	21.05	53.64	87.50
360	1.42	5.63	35.76	58.03	–
480	1.60	11.76	43.75	–	–
600	1.72	12.69	–	–	–
720	2.40	20.44	–	–	–
840	2.50	20.63	–	–	–

Figure 6 Plot of the dolomite dissolution data according to shrinking core model with surface reaction kinetics.

The specific surface areas decreased as the time increased due to shrinkage of the solid parts, and disappearance of the finest particles (Fig. 5). At 20 and 35 °C, the leaching continued longer and did not approach the equilibrium even over the 14 min period. However, at 50 and 65 °C, the surface areas of the samples reduced sharply and did not change much after 4 min, whereas at 80 °C the dissolution was almost complete.

The rates observed in the present study and those observed in experiments conducted by earlier researchers are in general agreement.[8] An experimental result obtained in another work[3] was different, however, because they used a disk sample which possibly had different crystal imperfections at the surface that was in contact with the acid solution. On the other hand, the surface area used in calculation of the dissolution rate was taken as constant although the leaching periods increased. However, the surface area used in this study was obtained as different at each experimental period.

3.7. Kinetic Analysis

The reaction stoichiometry of dolomite dissolving in hydro-chloric acid is:[1,6]

$$CaMg(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + MgCO_3 + H_2O + CO_2\uparrow \qquad (3)$$

$$MgCO_3 + 2H^+ \rightarrow Mg^{2+} + H_2O + CO_2\uparrow \qquad (4)$$

Reaction (3) is rapid and the rate of dissolution is controlled by the rate of reaction (4). Comparison of the scanning electron microscope photographs of the ore and the leach residue showed large difference in their sizes. This suggests that the dissolution process proceeded according to the shrinking core model. Hence, two established kinetic models may be considered for small particles. If the process is diffusion-controlled, Eq. (5)[9–11] is used:

$$t = \left[1 - (1 - X_B)^{2/3}\right]\frac{\rho_B \Psi R_0^2}{2bDC_0} \qquad (5)$$

where X_B is the converted fraction, ρ_B is the molar density, Ч is the mole fraction, R_o is the average radius of the solid particles, b is the stoichiometric coefficient, D is the molar diffusion coefficient and C_o is the bulk acid concentration.

If it is controlled by resistance of chemical surface reactions, then Eq. (6) is used:

$$t = \left[1 - (1 - X_B)^{1/3}\right]\frac{\rho_B R_0^2}{bk_s C_0} \qquad (6)$$

where k_s is the rate constant for the surface reaction.

Kinetic evaluation of reactions (3) and (4), which occurred during the hydrochloric acid leaching of the dolomite, indicates that these types of reactions do not conform with the diffusion kinetic model (Eq. 5) given above in the dissolution, because the curves obtained by using this model were not precise and did not give a perfect straight line for the data obtained. However, the chemical surface reaction model (Eq. 6) was more suitable than the model given in Eq. (5).

As shown in Fig. 6, the data obtained fit the model well. From the results of the statistical analysis, it was determined that the dissolution of the dolomite ore sample in hydrochloric acid was mostly controlled by chemical reaction. It may be written as the integral rate expression obeyed by the following equation:

$$1 - (1 - X_B)^{1/3} = kt \qquad (7)$$

Eq. (7) yields the straight lines from which the overall rate constants (k) can be obtained. The rate constants are calculated from the slopes of these curves.

The relation between the overall rate constant from Eq. (6) and temperature may be expressed by the Arrhenius equation:

$$k = A\exp(-E_a/RT) \qquad (8)$$

where k is the overall rate constant (s^{-1}), A is the frequency factor (s^{-1}), E_a is the activation energy (kJ mol^{-1}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is the reaction temperature (K).

The activation energy of 31.98 kJ mol^{-1} was calculated from the slope of the curve obtained by plotting the ln k values versus the reciprocal temperatures (Fig. 7). This was relatively low in comparison with the activation energies obtained by other workers. For example, the activation energy for dolomite dissolution in hydrochloric acid was found[1] to be 62 kJ mol^{-1}. It may stem from lithologic differences. It was reported by other researchers that the apparent activation energy depended on crystallinity. Preferential dissolution took place at grain boundaries of finely crystalline samples. This enhances dissolution and possibly decreases the activation energy of dolomite dissolution. Other researchers obtained an activation energy of 32 kJ mol^{-1} by using a stirring speed of 225 rpm.[3] Moreover, the activation energies were determined by the researchers as 15 kJ mol^{-1} for pH_{surf} 5 and 40 kJ mol^{-1} for pH_{surf} 1 respectively in the temperature range from 25 to 80 °C.[4]

4. Conclusions

Leaching of the dolomite sample in hydrochloric acid was studied by using a stirrer. The experiments were conducted over a wide range of conditions: the acid/dolomite mole ratio varied between 1.656 and 4.980; the solid/liquid ratio was changed from 15 to 55%; particle sizes of the samples were in the range of
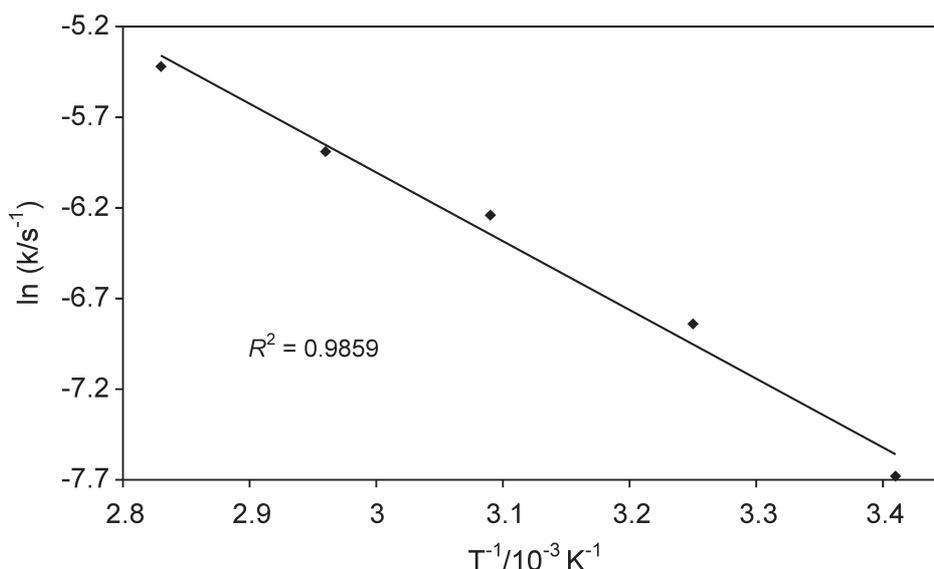
Figure 7 The Arrhenius curve obtained for the dissolution of the dolomite ore.

75–2000 μm; the stirrer speed was set from 50 to 250 rpm; and the runs were carried out at temperatures of 20, 35, 50, 65 and 80 °C for periods of 1–14 min.

The dissolution recoveries increased with increasing acid/dolomite mole ratio as the period of time proceeded. An inverse relationship was observed between the extraction recovery and the solid/liquid ratio. On the other hand, the larger the surface and interfacial areas in contact with the undersaturated leach solution, the higher the recovery reached. As a result, the smaller particles dissolved faster. The stirring speed became a less important factor at low temperatures.

In terms of the reaction temperature, it is shown that dissolution was very sensitive to the temperature in the range of 50–80 °C. The dissolution rates increased with increasing elapsed periods at all temperatures, but at higher temperatures faster dissolution was reached. This means that the transport control of the dolomite dissolution increases with increasing temperature. The dissolution kinetics accords with a shrinking core model with a surface chemical reaction as the rate-controlling step. The apparent activation energy of the dissolution depends on both the temperature and the hydrodynamic conditions.

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