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LEACHING OF MERSIN/AYDINCIK DOLOMITE ORE IN HYDROCHLORIC ACID. DISSOLUTION RATES

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Abstract: In this paper dissolution of dolomite ore, collected from Mersin/Aydincik in Turkey, was investigated under various experimental conditions in the presence of HCl acid. Particle size, acid/dolomite ratio, solid/liquid ratio, stirring speed, reaction time and temperature were also conducted to the determin the optimum experimental conditions. During the experiment, CO_2 amount released from the dolomite was measured through the experimental apparatus to determine reaction orders and rate constants of the sample at the different temperatures by using the fractional life approach method. It was found that, reaction orders and rate constants, based on temperatures, changed from 1.505 to 1.339 and between 3.17 and 10.49 10^{-2} mol dm^{-3} sec^{-1} respectively. In addition, differences in reaction rate constants were examined with the Arrhenius equation and activation energy of the dissolution process was calculated as 16.69 kJ mol^{-1}, which was consistent with the activation energies determined in literature.

Keywords: *dolomite leaching, CO_2 storage, fractional life method*

Introduction

Dolomite is a double carbonate ($CaCO_3 \cdot MgCO_3$) with variable amounts of impurities. It is used in many industrial and agricultural areas including construction, refractory, iron and steel making, glass making, filler applications in paints, plastics, rubbers and as a solid conditioner in agriculture due to its chemical composition. Also, dolomite is a good alternative source for production of pure magnesia (MgO) and many studies have been conducted for this purpose (Lingling and Deng, 2005; Galai et al., 2007; Otsuka, 1986; Samtani et al., 2001; Beruto et al., 2003; Hashimoto et al., 1980; Yildirim, 2008; Li et al., 2013). In these studies, the following tests were carried out: (1) thermal decomposition and (2) acid leaching combined with pyrohydrolysis.

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In the thermal decomposition tests, dolomite ore is heated at various temperatures in the presence of different CO_2 pressures in order to decompose dolomite to MgO and CaO. The second test consists of three stages including leaching, carbonization, and pyrohydrolysis. First, dolomite is dissolved easily by HCl acid in the leaching stage and calcium ions precipitatas as calcium carbonate (PCC). Purified magnesium-rich solution is obtained after solid/liquid separation in a carbonization stage (Yildirim, 2008; Li et al., 2013). PCC is used as filling and coating materials in paint, paper, plastic, pigment, ceramic and other industries (Yu et al., 2006; Matsumoto and Fukunaga, 2010). However, the properties of PCC have critical importance and influence the usage area and these properties can be controlled easily by production conditions.

As mentioned above, dissolution of dolomite with HCl acid is the first stage of production of MgO from dolomites. For this purpose, dissolution properties of the dolomite ore, obtained from Mersin/Aydincik, were investigated under different experimental conditions using the HCl acid leaching method.

Yildirim (2008) and Baba (2014) suggested that the shrinking core model, diffusion controlled method or chemical surface reaction model were useful for determination of kinetic behaviors of dolomite in acid solution, whereas dissolution kinetic orders and rate constants of dolomite at various temperatures were determined through the fractional half-life approach, which uses CO_2 amount remained in the sample versus time data. In the end, the purity of CO_2 content, released during leaching was determined and stored in order to use for precipitating Ca^{2+} ions as PCC in the future study.

Material and methods

Material

The sample used in the leaching experiments was obtained from the Mersin/Aydincik area in Turkey. Prior to the leaching experiments, approximately 20 kg of the sample was ground below 5 mm and analyzed using a Rigaku Miniflex II X-Ray diffractometer and a Panalytical X-Ray fluorescence spectrometer. In addition, a thin section was prepared to evaluate the sample under a polarizing microscope. It was understood that the sample consisted of dolomite mineral according to the microscopic examination and XRD analysis as shown in Fig. 1. The chemical content of the sample is given in Table 1.

Methods

The schematic of the experimental set-up, operated in a closed system, designed for this study is illustrated in Fig. 2. It consisted of four parts: Teflon coated mechanical stirrer, leaching tank (0.25 dm^3), gas collection column scaled (50 cm in height, 7.5 cm in inner diameter) and a water pool.

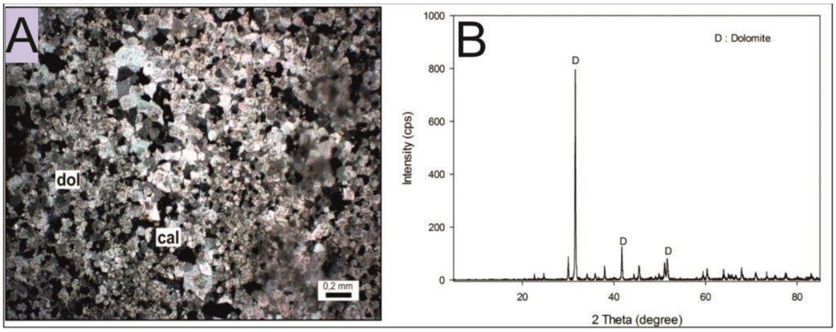

Fig. 1. Thin-section photograph (A) under microscope and XRD pattern (B) of the sample

Table 1. The chemical composition of the sample used in the leaching experiments

Element	MgO	CaO	Fe_2O_3	PbO	SiO_2	MnO
Grade (%)	22.84	32.37	0.42	0.019	0.17	0.009
Element	Al	As	Cd	Cr	Cu	Ni
Grade (ppm)	357.03	0.69	0.72	1.11	0.21	20.04
Element	Zn	Na	K	Loss of ignition: 44.30 %		
Grade (ppm)	6.09	15.23	8.34			

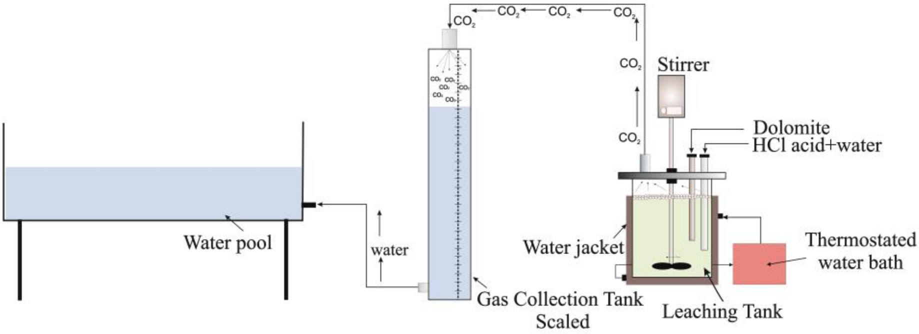

Fig. 2. Experimental set-up for dissolution of dolomite ore

The reaction temperature in leaching tank was controlled within the circulated thermostatic water bath. An amount of the released CO_2 gas, which went to gas collection tank from the leaching tank, was determined based on the downward displacement of acidified (0.1 M HCl) water. The reason for using acidified water was to prevent the neutralizing of CO_2 released in leaching experiments with water. The volume of measured CO_2 was converted to the volume at standard temperature and pressure. Additionally, amounts of the water vapor released in leaching experiments at various temperatures were calculated based on the pressure of the water vapor. Therefore, the net CO_2 volume released from dolomite leaching was obtained by considering the volume of the water vapor.

In the each test, 25 g of the sample was poured into the leaching tank under different experimental conditions, which were: particle size from –5.00 mm to –1.00 mm, acid/dolomite ratio from 3.50 to 6.00, solid/liquid ratio from 5.00% to 30.00%, reaction time from 1 minutes to 24 minutes, stirring speed from 0 rpm to 300 rpm, and reaction temperature from room temperature to 85 °C, respectively. However, only 5 g of the sample was used in the experiments at various temperatures for the determination of the reaction order and rate constant. The chemical equation of dissolution of dolomite with HCl acid is formulated in Eq. 1.

$$\mathrm{CaMg(CO_3)_2 + 4HCl + H_2O \longrightarrow CaCl_{2_{(aq)}} + MgCl_{2(aq)} + 3H_2O_{(l)} + 2CO_{2(g)}(\uparrow)} \quad (1)$$

Dissolution rates of dolomite components in water presence of HCl acid were high. When the predetermined reaction time ended, 200 cm^3 of pure water was poured into the leaching solution in order to reduce the concentration of HCl in solution.

At the end of the leaching tests, the solution containing insoluble impurities was filtered using Whatman (0.45 µm) filter paper. Ca^{2+} and Mg^{2+} contents in the solution obtained after the filtration was determined using a Perkin Elmer 900H Atomic Absorption spectrometer and the wet chemical analysis method.

Results and discussion

Effects of leaching parameters on the dolomite dissolution

The extraction recoveries of the Mg^{2+}, Ca^{2+}, Fe^{2+} and CO$_2$ of the samples, –5.00 mm, –3.15 mm, –2.80 mm, –2.00 mm and –1.00 mm in size are shown in Figure 3. Other experimental conditions were selected as a solid/liquid ratio 25%, reaction time 16 minutes, stirring speed 150 rpm, and acid/dolomite ratio 4. As shown in Fig. 3, a decrease in the particle size of the sample leads to increasing extraction recoveries. However, it was observed that Mg^{2+} extraction recovery was lower than that of the Ca^{2+} and CO$_2$ when the particle size was –3.15 mm or –5.00 mm.

It was understood from Fig. 3 that when the particle size of the sample was below 2.80 mm, the extraction recoveries of the Mg^{2+}, Ca^{2+}, and CO$_2$ were determined as 94.30%, 97.95% and 95.97%, respectively. However, extraction recovery was 62.64% for Fe^{2+} and this value increased within decreasing particle size of the sample. For this purpose, there was no need to reduce the size of the sample under 2.80 mm and the optimum particle size for this study was determined as < 2.80 mm. Particle size distribution of the sample –2.80 mm in size is shown in Fig. 4.

The sample –2.80 mm in size was leached by different HCl acid concentrations at the room temperature for 16 minutes. The solid/liquid ratio and stirring rate were chosen as 25% and 150 rpm, respectively. It was observed that the acid/dolomite ratio in the leaching test was an effective parameter as illustrated in Fig. 5.

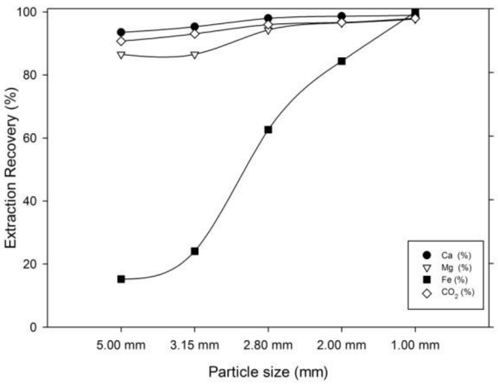

Fig. 3. The effects of particle size on dolomite dissolution

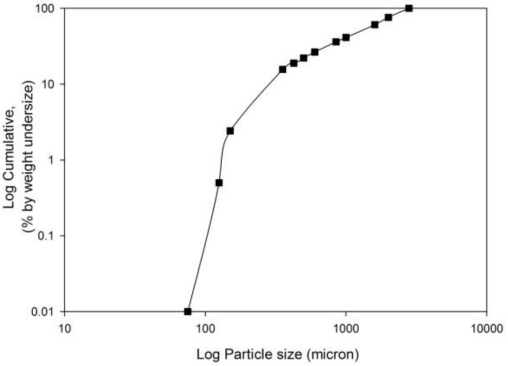

Fig. 4. Particle size distribution of the sample –2.80 mm in sized

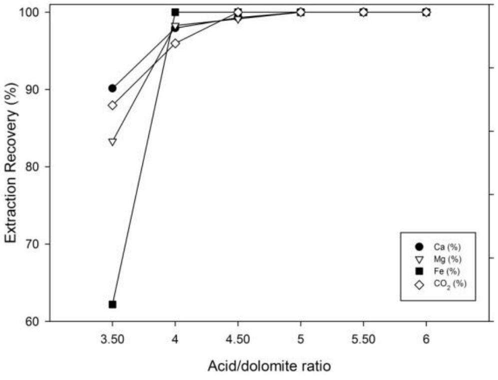

Fig. 5. Effects of acid/dolomite ratio on dissolution recovery of the sample

Some researchers pointed out that there was a difference between hydration degrees of Mg^{2+} and Ca^{2+}. These differences lead to obtaining different extraction recoveries. At the lowest acid/dolomite ratio, extraction recoveries of the Mg^{2+} and Ca^{2+} were 83.29% and 90.14%, respectively. These results were consistent with the literature (Yildirim, 2008). The dissolved amounts of the sample increased with the increasing acid/dolomite ratio. When the acid/dolomite ratio was adjusted to 5.00 or higher value, Mg^{2+} Ca^{2+} Fe^{2+} and CO_2 extraction recoveries were 100.00%. However, the optimum acid/dolomite ratio was selected as 4.50 due to the fact that extraction recoveries of Mg^{2+} Ca^{2+} Fe^{2+} and CO_2 were almost the same compared to the higher acid/dolomite ratios.

Six experiments were conducted in order to determine the effects of solid/liquid ratio on the extraction recoveries of the sample –2.80 mm in size at the room temperature and 150 rpm, for 16 minutes. An amount of the sample and acid/dolomite ratio that were kept constant during the experiments, whereas the amount of water added to solution changed in order to prepare desired solid/liquid ratio. Hence, the total volume of the solution was different for each experiment and the approximate amount of water needed in these experiments was given in Table 2.

Table 2. The necessary total volume of solution at various solid/liquid ratios

Solid/liquid ratio (%)	An amount of sample (g)	Total volume of solution (cm^3)	HCl acid (cm^3)	An amount of water necessary (cm^3)
5	25 g (0.14 mol)	475	52.25 cm^3 (0.63 mol)	422.75
10		225		172.75
15		141		89.40
20		100		47.77
25		75		25.00
30		58.33		6.08

It is obvious that extraction recovery of the sample depends on the solid/liquid ratio as shown in Fig. 6. Although thde acid/dolomite ratio was kept constant for each experiment, the strength of the acid and the amount of acid contacted per surface area of the sample decreased due to increasing the total volume of the solution. Therefore, the lowest extraction recoveries of Mg^{2+}, Ca^{2+}, Fe^{2+} and CO_2 were determined as 67.89%, 73.85% and 69.09%, when the solid/liquid ratio was 5%. The better extraction recoveries of Mg^{2+}, Ca^{2+}, Fe^{2+} and CO_2 were obtained at the higher solid/liquid ratios because of decreasing of water amount in solution. However, it was observed that stirring of the solution was difficult when the solid/liquid ratio was 30%. Thefore, the optimum solid/liquid ratio was selected as 25%.

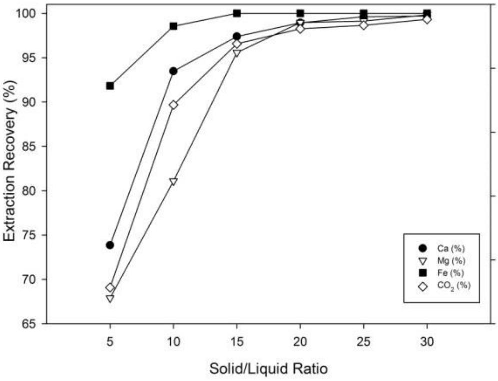

Fig. 6. Effect of solid/liquid ratio on sample dissolution recovery

In order to determine the effects of the reaction time on the dissolution rates of the sample –2.80 mm in sized, leaching tests were carried out at the nine different reaction times. The other experimental parameters were selected as 25% for solid/liquid ratio, 4.5 for acid/dolomite ratio and 150 rpm for stirring speed. Figure 7 shows that the reaction time was the effective parameter to obtain higher extraction recoveries of Mg^{2+}, Ca^{2+}, Fe^{2+} and CO_2. However, extraction recoveries of Mg^{2+}, Ca^{2+}, Fe^{2+} and CO_2 were different up to 8 minutes. Mg^{2+} extraction recovery was very low. Probably it depended on the hydration degree of Mg^{2+}. This result is in good agreement with the previous works (Yildirim 2008; Lund et al., 1973; Busenberg and Plummer, 1982; Herman and White, 1985; Gautelier et al., 1999; Akarsu, 2004; Chou et al., 1989). An increase in dissolution ratios showed a similar trend for Mg^{2+}, Ca^{2+}, Fe^{2+} and CO_2 provided that reaction time was 8 minutes or more. The dissolution rates tended to slow down after 12 minutes. The difference in dissolution ratios for the sample obtained at longer time than 16 minutes were very low. Therefore, the optimum reaction time of the sample conducted at the room temperature was determined as 16 minutes.

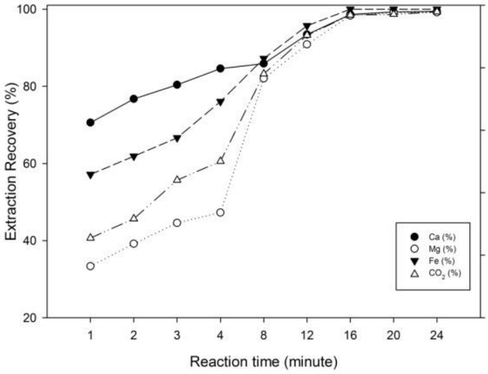

Fig. 7. Effect of reaction time on sample dissolution recovery

Figure 8 shows the effect of stirring speed on the dissolution rate of the sample – 2.80 mm in size at the constant experimental parameters: acid/dolomite ratio 4, solid/liquid ratio 25% and reaction time 16 minutes. It can be seen from Fig. 8 that the stirring speed was an effective parameter of dolomite dissolution.

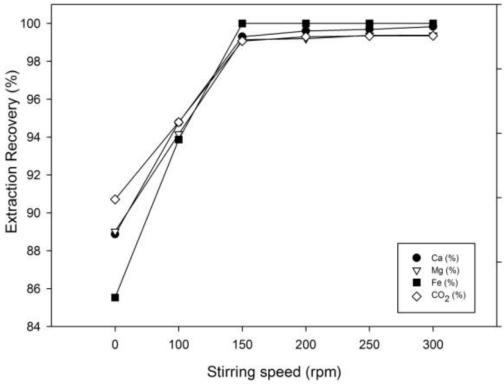

Fig. 8. Effect of stirring speed on sample dissolution recovery

The extraction recoveries of Mg^{2+}, Ca^{2+}, Fe^{2+} and CO_2 were lower without stirring. As shown in Fig. 8, their dissolution rates of increased with stirring, up to 150 rpm, and there were no changes in the extraction recoveries for experiments conducted at higher stirring speeds. The optimum stirring speed for this study was selected as 150 rpm. Figure 9 shows that the solution temperature increased up to 27 °C, from 20 °C during the experiment, due to the fact that the dissolution of the sample with HCl acid was an exothermic reaction.

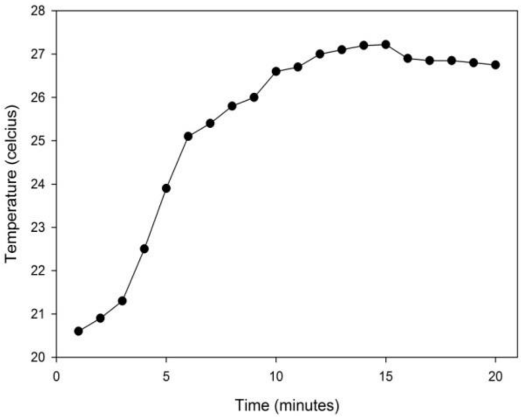

Fig. 9. Change of solution temperature versus time

Hosgun and Kurama (2012) indicated that the dissolution rate of the sample was affected by the reaction temperature and the sample was dissolved easily at higher temperatures in shorter time. The dissolution behavior of the sample at various reaction temperatures (room temperature, 33 °C, 40 °C, 55 °C and 85 °C) were examined in accordance with this purpose. A series of the experiments were conducted at the constant experimental conditions. Reaction time, stirring speed, solid/liquid ratio and acid/dolomite ratio were selected as 4 minutes, 150 rpm, 25% and 4.5, respectively. Figure 10 shows that reaction temperatures accelerated dissolution of the sample. When the results obtained from the experiments conducted for 4 minutes at different temperatures were examined, it was determined that all of Mg^{2+}, Ca^{2+}, Fe^{2+} and CO_2 in the sample dissolved easily at 55 °C or for over 4 minutes, compared to the lower reaction temperatures. It can be said that reaction time was influenced by the temperatures and reaction took a long time at room temperature, whereas higher dissolution rates within shorter times were obtained at the higher temperatures.

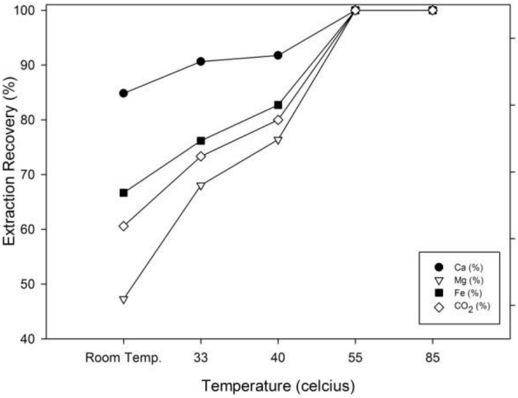

Fig. 10. Effect of temperature on sample dissolution

Dissolution rates

In order to the determine the dissolution rate of a sample, the change in concentrations should be measured. The rate of a chemical reaction depends on concentration of reactants or products obtained during the experiment. The fractional half-life method can be useful and reduction of CO_2 amount in the sample versus the leaching time can be measured easily through operating in a closed system. The amount of CO_2 remained in the sample against time were recorded and evaluated by the fractional half-life method to determine the reaction order of dissolution of the sample at the different temperatures.

The fractional half-life method can be extended to any fractional life method where the concentration of reactant decreases to any fractional value ($F = C_A/C_{A0}$ at a time t_F). The reaction order is determined with the help of a plot of $\log_{tF}$ versus $\log C_{Ao}$. It is described by Eq. 2 (Levenspiel, 1999).

$$\log t_F = \log\left(\frac{F^{1-n}-1}{k(n-1)}\right) + (1-n)\log C_{A0} \tag{2}$$

where t_F is the time difference, F fractional life ratio, n reaction order, k reaction rate constant, C_{A0} = the content remained in the sample at a certain time.

In order to determine the reaction order and rates of dissolution of dolomite at different temperatures, a series of experiments were carried out. The other parameters were kept constant: particle size –2.80 mm, acid/dolomite ratio 4.5, stirring speed 150 rpm. The experimental data, for determination reaction order and rate constants, obtained at different temperatures, are shown in Table 3.

Table 3. CO_2 amounts remained in sample after leaching experiments at different temperatures

20°C		33°C		40°C		55°C		85°C	
Time (s)	CO_2 content (10^{-2} mol)	Time (s)	CO_2 content (10^{-2} mol)	Time (s)	CO_2 content (10^{-2} mol)	Time (s)	CO_2 content (10^{-2} mol)	Time (s)	CO_2 content (10^{-2} mol)
0	5.25	0	5.25	0	5.25	0	5.25	0	5.25
38	3.99	45	2.94	40	2.94	30	2.94	18	2.94
72	3.15	90	1.89	82	1.89	62	1.89	35	1.89
163	1.89	125	1.26	186	0.63	145	0.63	70	0.63
252	1.26	201	0.63	370	0	250	0	135	0
468	0.63	440	0						
684	0								

Figure 10 shows that the increases in reaction temperatures lead to a decrease of the reaction times. At 85°C, the total dissolution time of the sample was 135 seconds, whereas all samples dissolved slowly and took a long time at 20 °C.

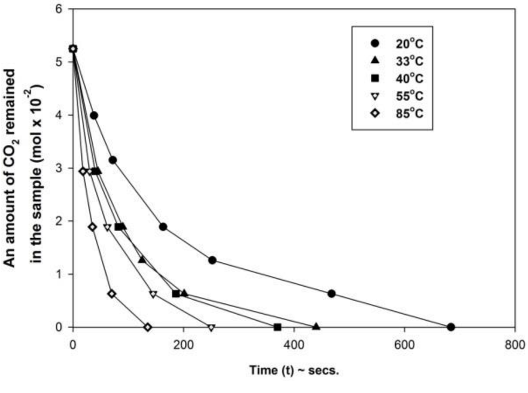

Fig. 10. CO_2 amount remained in sample after leaching experiments at various temperatures

The procedure of the fractional half-life approach method is as follows: fractional life ratio ($F = C_A/C_{A0}$) selected as 80% was applied for prediction of CO_2 amount remained within any time in the leaching experiments. The 80% values of the experimental results obtained at any time at room temperature was determined from the curve illustrated in Fig. 11. Additionally, the elapsed time was recorded as t_F. For example, it was determined that the amount of CO_2 in the sample decreased to $4.20 \cdot 10^{-2}$ mol which corresponds to 80% of the initial CO_2 in the sample when the elapsed time was 33 seconds (t_F) in the leaching experiment conducted at the room temperature. The junction point of these values was marked as A on the curve. Likewise, junction points belonging to other values obtained from Fig. 11 were marked as B, C, D, E and F on the curve, respectively. The experimental results and values determined from Fig. 11 are given in Table 4.

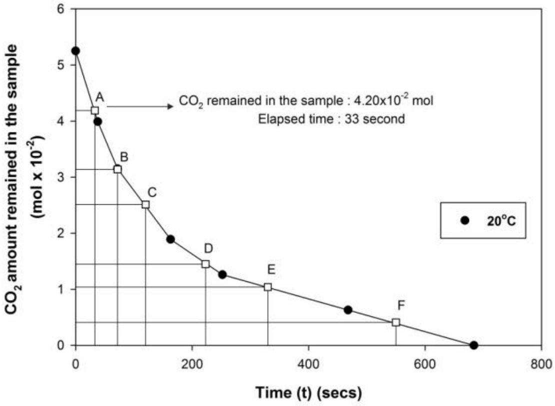

Fig. 11. Determination of CO_2 amount ($0.8 \cdot C_{A0}$) from the curve

Table 4. Results obtained in experiment conducted at room temperature

from experiments		from curve					
CO_2 content (10^{-2} mol) (C_{A0})	Time (s) (t_1)	CO_2 content (10^{-2} mol) ($0.8 \cdot C_{A0}$)	Time (s) (t_2)	Code	$t_F = t_1 - t_2$	log t_F	log C_{A0}
5.24	0	4.20	33	A	33	1.52	–1.28
3.99	38	3.15	72	B	34	1.53	–1.4
3.15	72	2.52	110	C	38	1.58	–1.5
1.89	163	1.47	223	D	60	1.78	–1.72
1.26	252	1.05	330	E	78	1.89	–1.9
0.63	468	0.42	550	F	82	1.91	–2.2
0	684						

Figure 12 illustrates logt_F versus logC_{A0}. The slope of the curve was used to determine the reaction order of dissolution of sample at room temperature. The reaction order was calculated using Eq. 3.

$$\text{Reaction order} = 1 - n \tag{3}$$

where, n is the slope of the curve shown in Fig. 12.

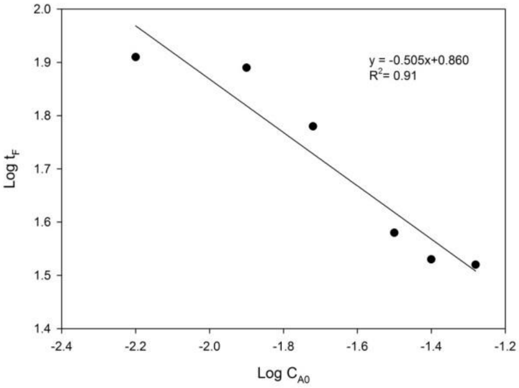

Fig. 12. logC_{A0} versus logt_F at room temperature

The reaction order and rate constant of dissolution of dolomite sample at room temperature were determined as 1.505 and $3.17 \cdot 10^{-2}$ mol·dm^{-3}·s^{-1} by using Eqs. 2 and 3. Other reaction orders and rate constants of the dolomite sample in the leaching experiment at other temperatures are listed in Table 4. The reaction rates of the sample in the leaching experiment increased with temperature and reaction order tends to decrease.

Table 4. Reaction orders and rate constants at various temperatures

Temperatures(°C)	Reaction order	Reaction rate constant (mol dm^{-3} s^{-1}) $\cdot 10^{-2}$
Room temperature	1.505	3.172
33	1.392	3.272
40	1.385	4.326
55	1.371	5.662
85	1.339	10.495

The variation of the reaction rate constants was examined by the Arrhenius equation:

$$\ln k = \ln A - (E/\mathrm{R}T) \tag{4}$$

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

Many researchers revealed that, activation energies of the dolomite dissolution process changed from 0.13 kJ mol^{-1} to 62.00 kJ mol^{-1} and these differences probably depended on crystalline properties of dolomite (Yildirim 2008; Baba et al., 2014; Lund et al., 1973; Herman and White, 1985; Gautelier et al., 1999; Akarsu and Yildirim, 2008). In this study, the activation energy of the dissolution process was calculated as 16.69 kJ mol^{-1} from the slope of the curve obtained by plotting ln k values against temperature as shown in Fig. 13.

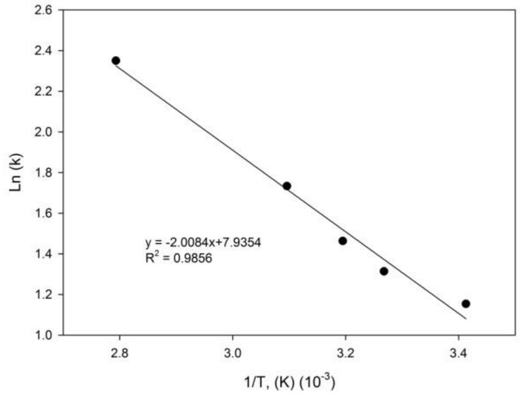

Fig. 13. The Arrhenius plot for dolomite dissolution at various temperatures

Conclusions

In this study, the dissolution of the dolomite sample with HCl acid at various experimental conditions was examined and research findings obtained in this study are as follows.

1. There was no need to crush sample below 2.80 mm due to the fact that extraction recoveries of the samples < 2.80 mm in size were almost the same.

2. The acid/dolomite ratio has a significant effect on extraction of dolomite. As the acid/dolomite ratio in leaching test increases, the extraction recoveries of the sample tend to increase.

3. An increase in the reaction temperatures caused an increase in the reaction rate constant of the sample dissolved within a shorter time at higher solution temperatures.

4. The fractional life approach is a useful method for evolution of dolomite dissolution at various temperatures.

5. The purity of CO_2 released in leaching experiment was determined as 99.10% by using CO_2 analysis equipment. It is thought that it will be used so for production of

precipitated calcium carbonate from the solution obtained from the leaching experiment in a next study.

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