CHAPTER IV
RESULTS AND DISCUSSION

4.1 Dissolution Rate of Analcime

4.1.1 Batch Experimental Results

The rate of dissolution of analcime was studied by digesting 2 g of analcime in 300 ml of HCl solution. The variables studied were temperature (25 and 45°C) and acid concentration (0.1-7 M). For the experiments at 25°C, the concentration of HCl solution was varied from 0.1 to 7 M. The dissolution curves of aluminum and silicon from analcime are shown in Figures 4.1 and 4.2. For the experiments at 45°C, the concentration of HCl solution was varied from 0.1 to 0.65 M. The dissolution curves of aluminum and silicon from analcime at 45°C are shown in Figures 4.3 and 4.4 (1^{st}, 2^{nd} and 3^{rd} shown in the figures denote the first, second, and third set of experiments carried out under the same conditions).

The rates of dissolution of aluminum and silicon were calculated from the slopes of linear fitting to the initial aluminum and silicon dissolved versus time for various acid concentrations. Table 4.1 shows the dissolution rates of aluminum and silicon from analcime in hydrochloric acid at 25°C and at 45°C.

The effect of HCl concentration on the rate of analcime dissolution was studied by varying HCl concentration from 0.1 to 7 M. The rates of dissolution of alumium and silicon from analcime at 25°C and 45°C are shown in Figures 4.1, 4.2, 4.3 and 4.4, respectively. The dissolution rate of aluminum increased with increasing the HCl concentration at 25°C and at 45°C. The dissolution rate of silicon with HCl concentrations in a range 0.1-4 M increased with increasing HCl concentration. However, the dissolution rate of silicon in 7 M HCl was lower than the rate in 4 M HCl because the mechanism of analcime dissolution with 7 M HCl was found to be the leaching of aluminum from zeolite matrix. Therefore, some silicon could be dissolved in acid solution while some silica remained as residue.

In the analcime structure, the covalent bonds between Si–O and Al–O are much stronger than the ionic bonds between cation (Na^+) and the lattice network. After leaching of the surface, Na^+ cation has been primarily removed, so, the network in the surface of the analcime will, then, contain the following groupings: Si–O–Si and Si–O–Al. When the network is being dissolved by the hydrochloric acid, these bonds must be broken for the release of silicon and aluminum into the solution.

Figures 4.5 and 4.6 show the rate of silicon dissolution versus the rate of aluminum dissolution at various HCl concentrations at 25°C and 45°C, respectively. The results showed that the molar ratios of the dissolution rates of silicon and aluminum were in the ratio 2:1 when concentration of HCl was in the range of 0.1-4 M. That is, the rate of removal of each of the elements within the lattice proceeded at the rate proportional to its lattice concentration. In contrast, the molar ratio of the dissolution rates of silicon and aluminum in 7 M HCl solution at 25°C was about 1:1. However, the rate was calculated based on the assumption that silicon did not rapidly precipitate, thereby, giving a false rate of dissolution. These results can be explained by Yang and Xu's research work. Yang and Xu (1997) suggested that the very high electron affinity of the HCl proton could induce the distortion of tetrahedral aluminum sites, which was also confirmed by the smaller Al–O–Si angle and the longer Al–O bond length when H^+ is located at cation sites. In other words, the framework of zeolite is deformed and influenced by the nature of compensating cations. Such a distorted structure of the AlO_4 tetrahedron has a great strain and is not stable; the Al–O bond in the framework is easily broken, thus, leading to the removal of aluminum from the matrix.

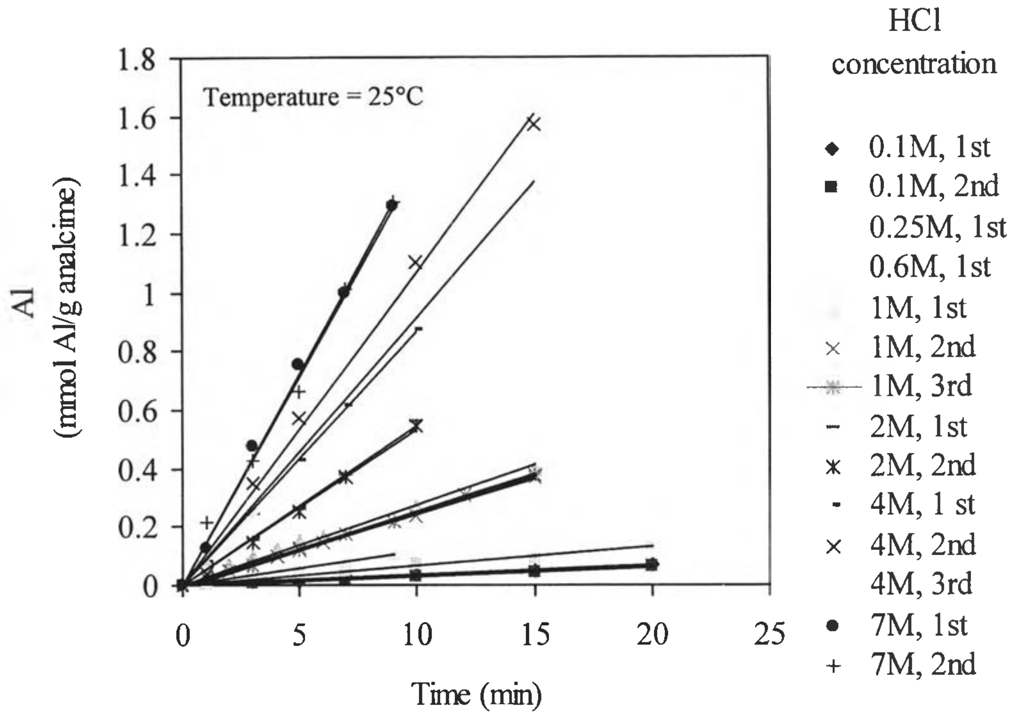

Figure 4.1 Dissolution of aluminum from analcime in 0.1- 7 M HCl at 25°C.

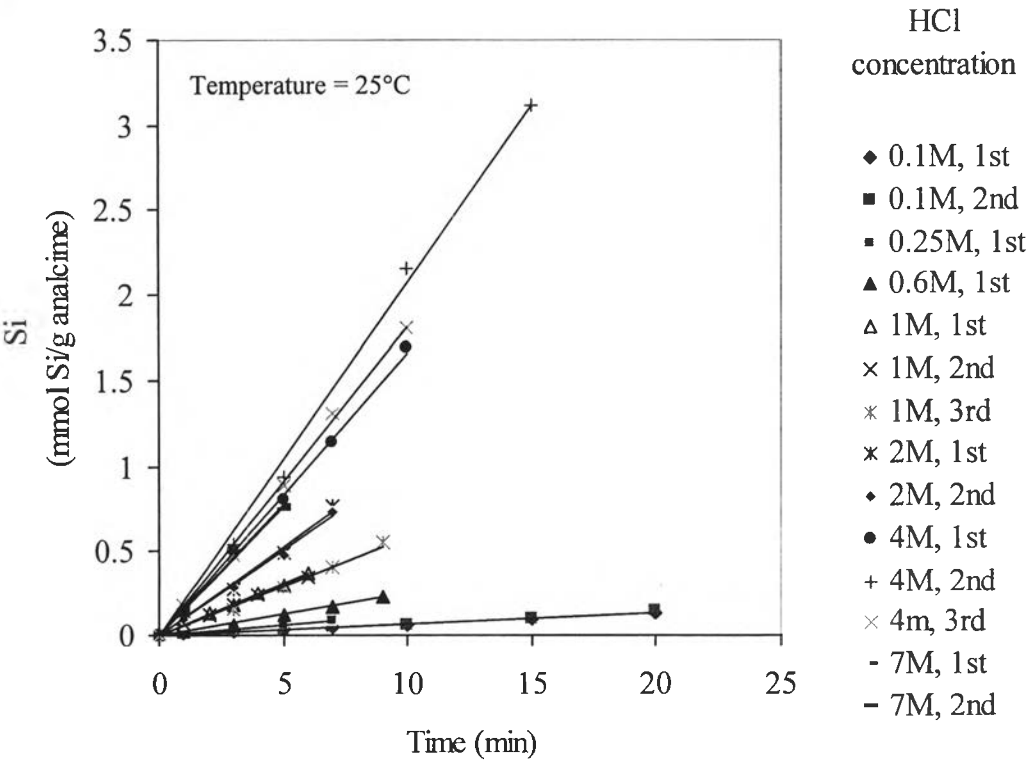

Figure 4.2 Dissolution of silicon from analcime in 0.1-7 M HCl at 25°C.

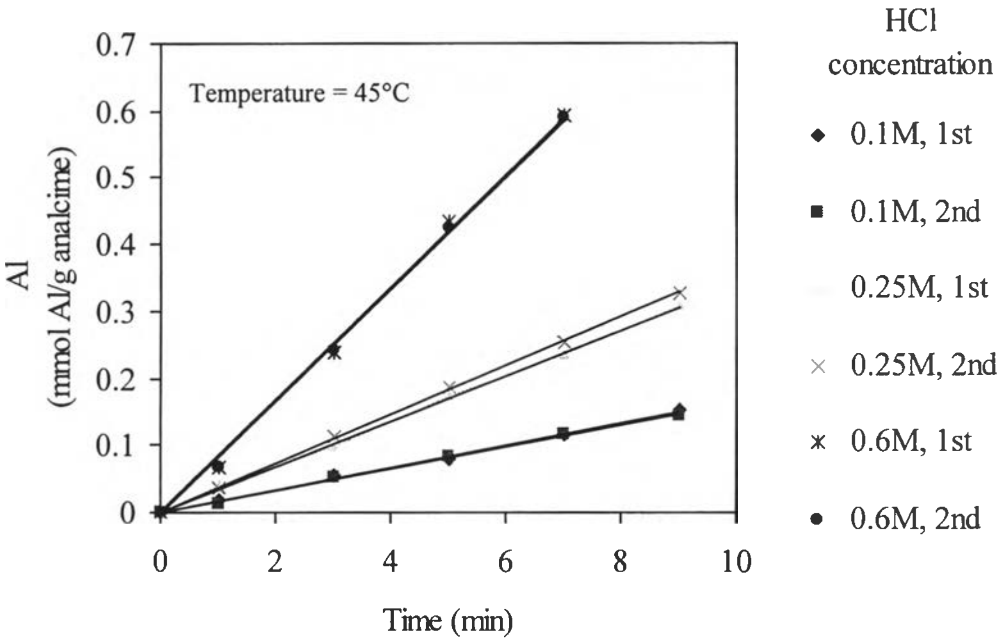

Figure 4.3 Dissolution of aluminum from analcime 0.1- 0.6 M HCl at 45°C.

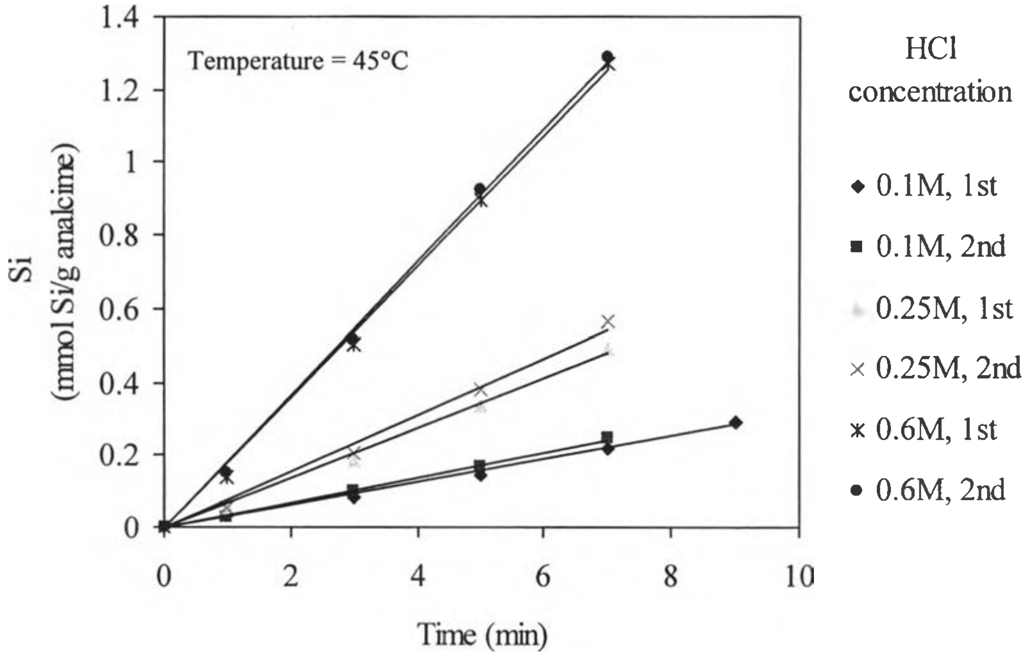

Figure 4.4 Dissolution of silicon from analcime in 0.1-0.6 M HCl at 45°C.

Table 4.1 Rates of analcime dissolution by HCl at 25°C and 45°C

Temperature (°C)	HCl concentration (mol/l)	$-r_{Al}$ (mol Al/g·min)	$-r_{Si}$ (mol Si/g·min)	$-r_{Si}/-r_{Al}$ *
25	0.1	3.40×10^{-6}	6.80×10^{-6}	1.97
		3.00×10^{-6}	8.10×10^{-6}	2.27
	0.25	6.60×10^{-6}	1.26×10^{-5}	1.91
	0.6	1.13×10^{-5}	2.48×10^{-5}	2.20
	1	2.75×10^{-5}	6.20×10^{-5}	2.25
		2.43×10^{-5}	5.96×10^{-5}	2.45
		2.49×10^{-5}	5.90×10^{-5}	2.37
	2	5.46×10^{-5}	1.04×10^{-4}	1.91
		5.30×10^{-5}	1.01×10^{-4}	1.91
	4	8.66×10^{-5}	1.66×10^{-4}	1.91
		1.07×10^{-4}	2.08×10^{-4}	1.94
		9.16×10^{-5}	1.81×10^{-4}	1.98
	7	1.45×10^{-4}	1.57×10^{-4}	1.08
		1.43×10^{-4}	1.52×10^{-4}	1.07
45	0.1	1.67×10^{-5}	3.15×10^{-5}	1.89
		1.63×10^{-5}	3.42×10^{-5}	2.10
	0.25	3.40×10^{-5}	6.85×10^{-5}	2.01
		3.66×10^{-5}	7.76×10^{-5}	2.12
	0.6	8.44×10^{-5}	1.79×10^{-4}	2.12
		8.39×10^{-5}	1.83×10^{-4}	2.18

* Stoichiometric dissolution = 2.0

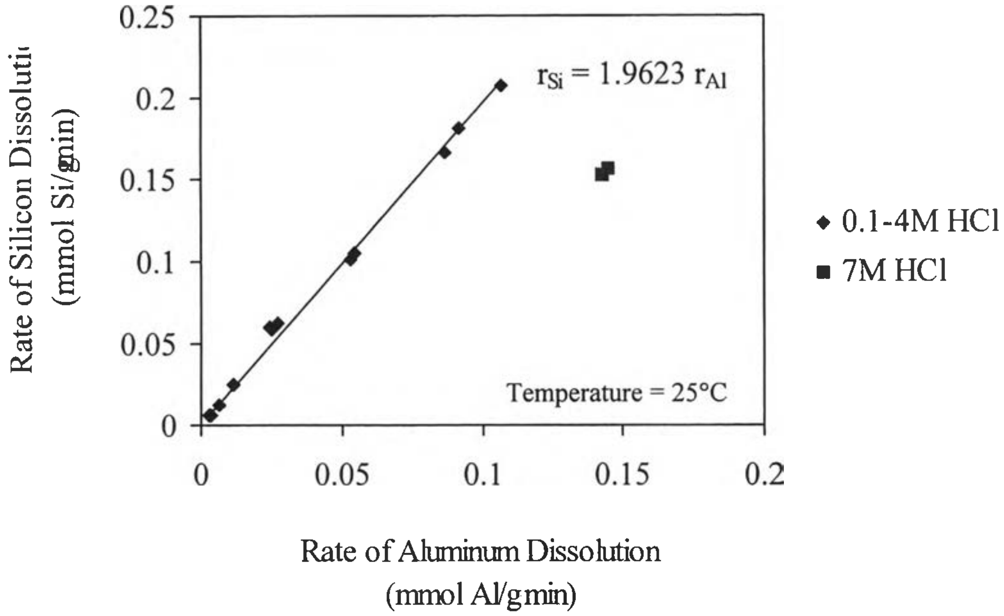

Figure 4.5 The rate of silicon dissolution versus the rate of aluminum dissolution in 0.1-7 M HCl at 25°C determined from batch reactor experiment.

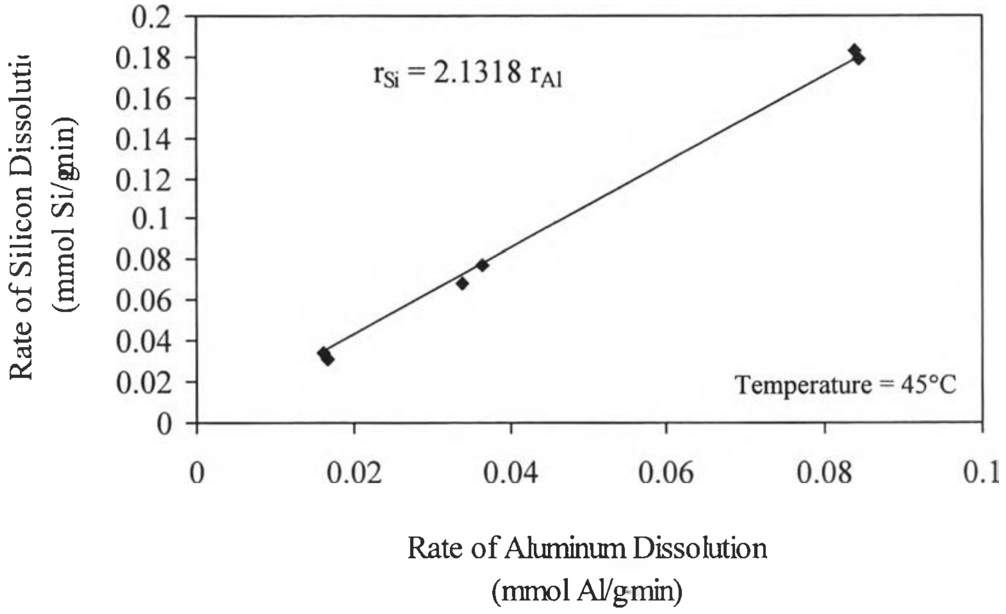

Figure 4.6 The rate of silicon dissolution versus the rate of aluminum dissolution in 0.1-7 M HCl at 45°C determined from batch reactor experiment.

For the dissolution of analcime in highly concentrated HCl (7 M), the analcime had low acid resistance. The mechanism of acid attack on analcime appeared to be leaching of aluminum from the zeolite matrix into the solution, so the framework of analcime was destroyed. Therefore, some silicon could be dissolved in the acid solution. In addition, when the zeolite matrix was destroyed, a significant amount of amorphous residue remained. Thus, the molar ratio of dissolution rates with respect to silicon and aluminum was not 2:1. It was concluded that complete decomposition and dissolution of the analcime matrix by 0.1-4 M HCl was observed, rather than preferential dissolution of aluminum. However, the attack of analcime by 7 M hydrochloric acid suggested a leaching reaction, whereby aluminum was preferentially leached.

4.1.2 Differential Experimental Results

The dissolution of analcime in 7 M HCl studied in a batch reactor was further carried out in a differential reactor. The rate of dissolution was studied using 7 M HCl solution and 0.2 g of analcime at volume metric flow rate of HCl solution of 10 ml/min. The experiment was carried out for 9 min at 25°C.

The dissolution rates of aluminum and silicon at various times under the highest HCl concentration of 7M are shown in Table 4.2. The results indicated that the molar ratio of dissolution rates with respect to silicon and aluminum was not proportional to their concentrations in the zeolite matrix (2:1). The attack of analcime by HCl is essentially a leaching process, in which aluminum is preferentially leached.

The particles remained in the differential reactor were analyzed by EDX to determine the composition of elements on the surfaces. The EDX spectrum is shown in Appendix. This spectrum indicated that there were only silicon and oxygen on the surface of matrix. It can be concluded that dissolution of the analcime matrix by 7 M HCl results in the formation of amorphous silica residue. These results are consistent with the batch experiment using 7 M HCl that aluminum was removed more rapidly from the matrix.

Table 4.2 Rates of dissolution of aluminum and silicon from analcime using the differential reactor using 7 M HCl solution with a flow rate of 10 ml/min at 25°C

Time (min)	$-r_{Al}$ (mol Al/g·min)	$-r_{Si}$ (mol Si/g·min)	$-r_{Si}/-r_{Al}$
0.5	1.49×10^{-4}	1.52×10^{-4}	1.02
1	1.47×10^{-4}	1.90×10^{-4}	1.30
1.5	1.47×10^{-4}	2.02×10^{-4}	1.37
2	1.42×10^{-4}	2.02×10^{-4}	1.43
2.5	1.38×10^{-4}	2.02×10^{-4}	1.46
3	1.38×10^{-4}	2.02×10^{-4}	1.46
3.5	1.38×10^{-4}	1.96×10^{-4}	1.38
4	1.38×10^{-4}	1.90×10^{-4}	1.38
4.5	1.38×10^{-4}	1.81×10^{-4}	1.31
5	1.38×10^{-4}	1.72×10^{-4}	1.25
5.5	1.38×10^{-4}	1.60×10^{-4}	1.16
6	1.31×10^{-4}	1.52×10^{-4}	1.16
6.5	1.28×10^{-4}	1.31×10^{-4}	1.03
7	1.28×10^{-4}	1.28×10^{-4}	1.00
7.5	1.24×10^{-4}	1.22×10^{-4}	0.98
8	1.19×10^{-4}	1.07×10^{-4}	0.90
8.5	1.19×10^{-4}	1.01×10^{-4}	0.85
9	1.19×10^{-4}	8.91×10^{-5}	0.75

4.2 Effects of HCl Concentration and Temperature on Analcime Dissolution

4.2.1 HCl Concentration Effect

Figures 4.7 and 4.8 show the plots of the dissolution rate of aluminum from analcime as a function of HCl concentration at 25°C and 45°C, respectively. These rates were determined from batch experiments. Figures 4.9 and 4.10 show the dissolution rate of silicon from analcime as a function of HCl concentration at 25°C and 45°C, respectively. It is observed that with a log-log plot between the dissolution rate and acid concentration, the relationship yields a straight line. It can be concluded that the leaching of aluminum from analcime takes place uniformly throughout the entire lattice.

Based on the experimental results, the rates of analcime dissolution can be expressed as following:

At 25°C $$-r_{Al} = 2.540\text{x}10^{-5}\ C_{HCl}^{0.92} \qquad (4.1)$$

At 45°C $$-r_{Al} = 1.306\text{x}10^{-4}\ C_{HCl}^{0.91} \qquad (4.2)$$

At 25°C $$-r_{Si} = 5.200\text{x}10^{-5}\ C_{HCl}^{0.92} \qquad (4.3)$$

At 45°C $$-r_{Si} = 2.283\text{x}10^{-4}\ C_{HCl}^{0.97} \qquad (4.4)$$

The unit of HCl concentration is mol/l and the dissolution rate is expressed in mol Al/g·min. From the calculated values of the reaction order and the kinetic constant, the dissolution rate of aluminum from analcime in HCl is adequately described by this form of the rate law:

$$-r_{Al} = kC_{HCl} \qquad (4.5)$$

The specific rate constants for the dissolution of aluminum from analcime in HCl at 25°C and 45°C were found to be 2.54 x10^{-5} and 1.306x10^{-4} mol Al/(g·min·HCl molarity), respectively.

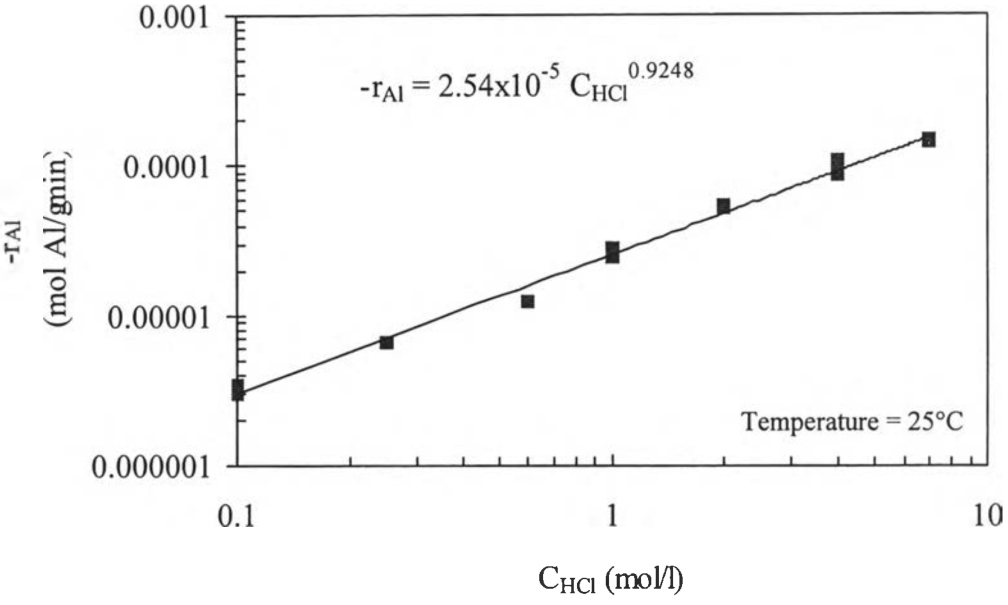

Figure 4.7 Dissolution rate of aluminum from analcime as a function of the concentration of HCl at 25°C.

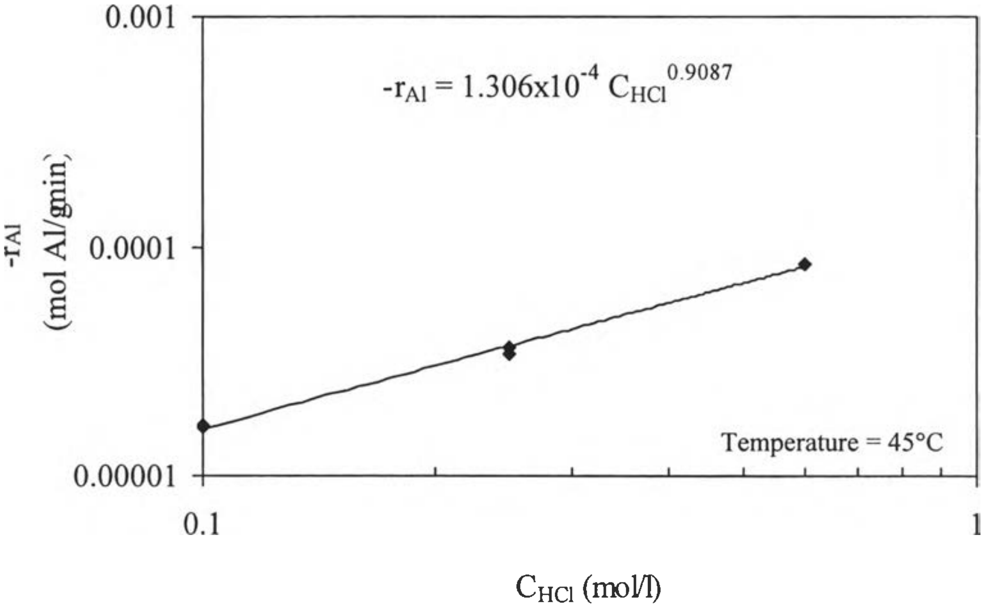

Figure 4.8 Dissolution rate of aluminum from analcime as a function of the concentration of HCl at 45°C.

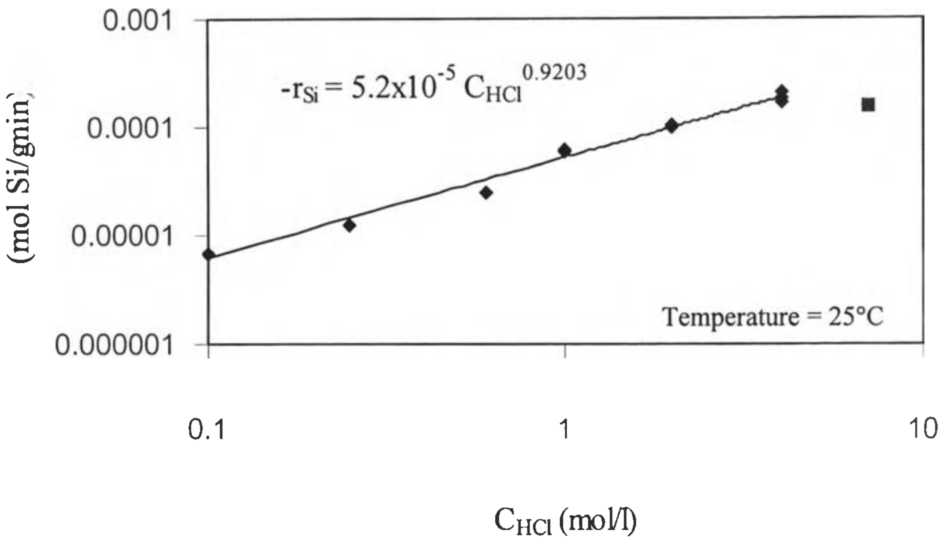

Figure 4.9 Dissolution rate of silicon from analcime as a function of the concentration of HCl at 25°C. (excluding the data at 7M HCl)

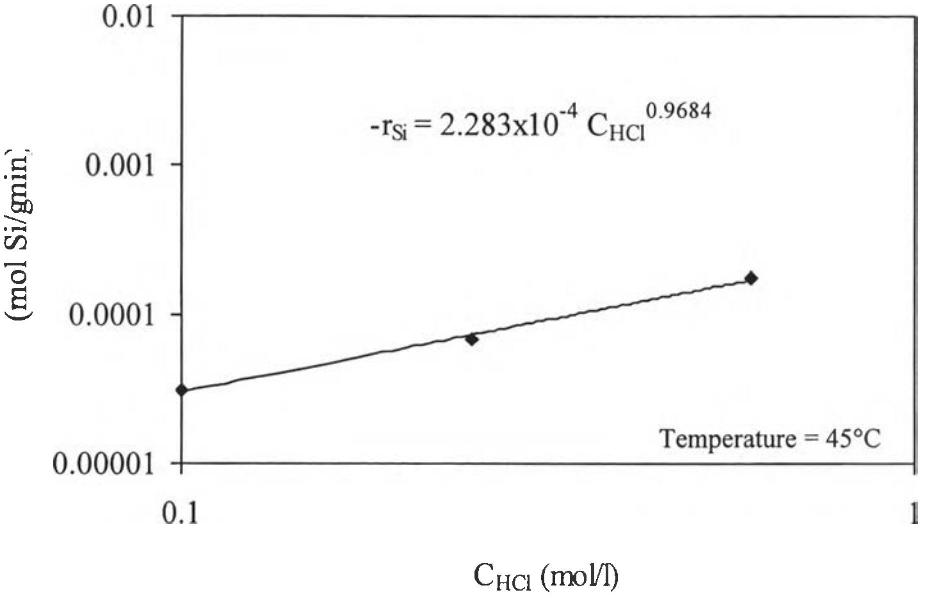

Figure 4.10 Dissolution rate of silicon from analcime as a function of the concentration of HCl at 45°C.

4.2.2 Temperature Effect

The effect of temperature on the rate of analcime dissolution was investigated by performing the experiments at two temperatures. The experiments were conducted at 25°C and 45°C. The rates of dissolution of aluminum and silicon from analcime at 25°C and 45°C are shown in Table 4.1. The results indicated that the dissolution rates of both aluminum and silicon at 45°C were much faster than the rates at 25°C. It was found that the dissolution rate of analcime in HCl increased significantly by increasing the temperature of HCl solution.

The specific rate constants at two different temperatures were used in determination of the activation energy of the dissolution. The quantitative relationship for the activation energy is given by the Arrenius equation.

$$k = A \exp(-E/RT) \qquad (4.6)$$

where k = specific rate constant (mol Al/(g·min·HCl molarity))

A = frequency factor or pre-exponential factor (a constant)

E = activation energy (Cal/mol)

R = gas constant = 1.987 Cal/mol·K

T = absolute temperature (K)

One can solve equation (4.6) for the activation energy proving k at two temperatures T_1 and T_2.

$$E = R \ln(\frac{k_2}{k_1})(\frac{T_1 T_2}{T_2 - T_1}) \qquad (4.7)$$

The activation energy for dissolution of aluminum from analcime in hydrochloric acid is approximately 15.43 Cal/mol.

4.3 Precipitation of Silicon

Figures 4.11 and 4.12 show the concentration profiles of aluminum and silicon in the solution as a function of time from analcime dissolution in 7 M and 4 M HCl solution, respectively. The curve of silicon in Figure 4.11 shows that the concentration of silicon in the solution rapidly increased until it reached the maximum value about 1×10^{-2} mol/l, at 10 min. After that, it slowly decreased to 2.5×10^{-3} mol/l and then it remained constant. The results indicated that some silicon dissolved in HCl solution precipitated out. As dissolution progressed, the solution becomes saturated with silica. Subsequent silica dissolved from the zeolite matrix then precipitates immediately from solution as amorphous silica in the form of a white pasty gel as observed in the experiments. This gel was characterized by energy dispersive X-ray spectroscopy (EDX) and fourier transform infrared spectroscopy (FTIR) as discussed in the next section. As can be seen from Figure 4.12, the concentration of silicon initially increases rapidly, then slowly until it reached the maximum concentration of 41×10^{-3} mol/l at 300 min and, then, slowly decreases with increasing the reaction time. After 24.5 h, the concentration of silicon in solution decreased to 19×10^{-3} mol/l.

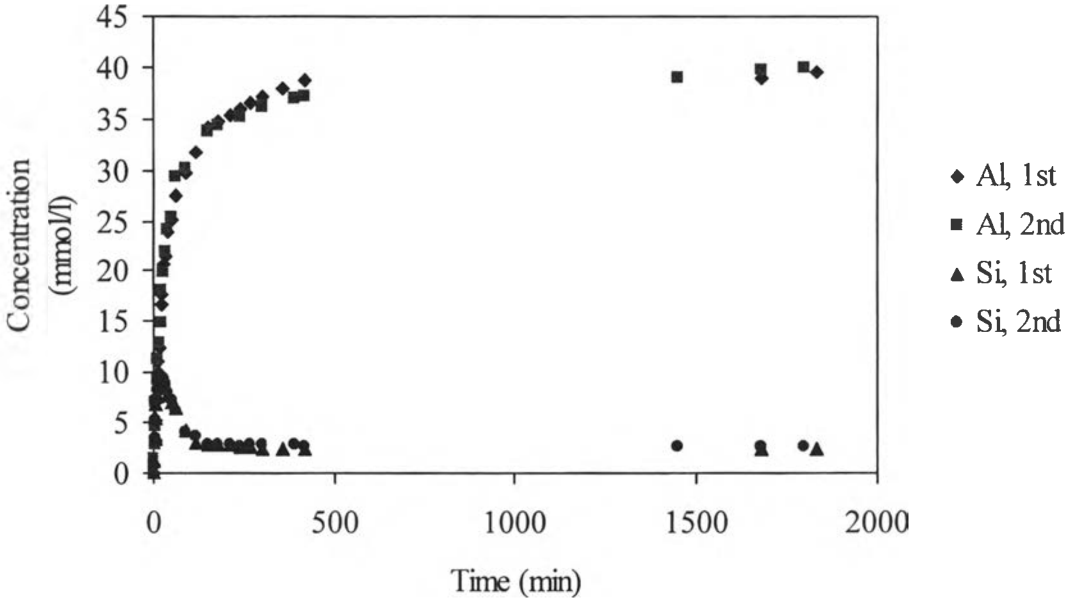

Figure 4.11 Concentration profiles of aluminum and silicon from analcime dissolution in 7 M HCl at 25°C.

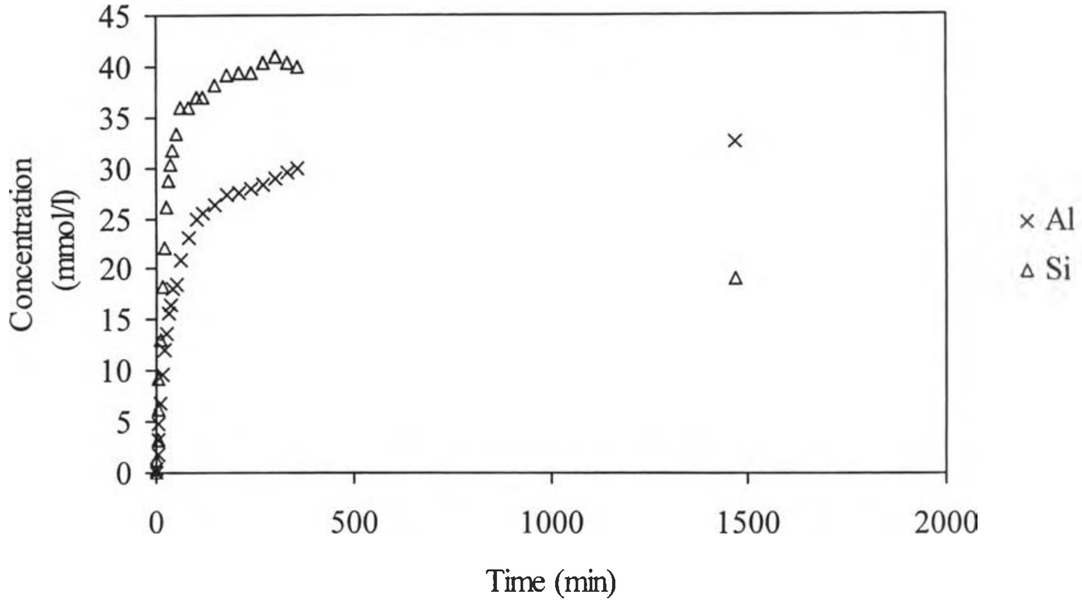

Figure 4.12 Concentration profiles of aluminum and silicon from analcime dissolution in 4 M HCl at 25°C.

4.4 Confirmation of Silica Gel Formation

The precipitates in form of white gel obtained from the experiments using 4 and 7 M HCl solutions were dried in the oven at 100°C. After drying, the dried precipitates were then characterized by atomic absorption spectroscopy (AAS) and energy dispersive X-ray analyzer (EDX). The AAS analysis results showed that only silicon was found in the gel samples. The EDX spectra showed only silicon and oxygen peaks. The analytical results clearly indicate that the gel precipitates obtained from the dissolution experiment were silica gel.

Fourier transform infrared spectroscopy (FTIR) was employed to identify the functional groups of silica gel precipitates obtained from the experiments using solutions 4 M and 7 M HCl. The silica gel precipitates were dried in an oven for 24 h at 100°C after which they formed a white powder. Next, these samples were mixed with KBr (IR grade) in a weight ratio of 1 to 45. The FTIR spectra of the white silica precipitates in form of powder are shown in Figures 4.13 and 4.14, respectively.

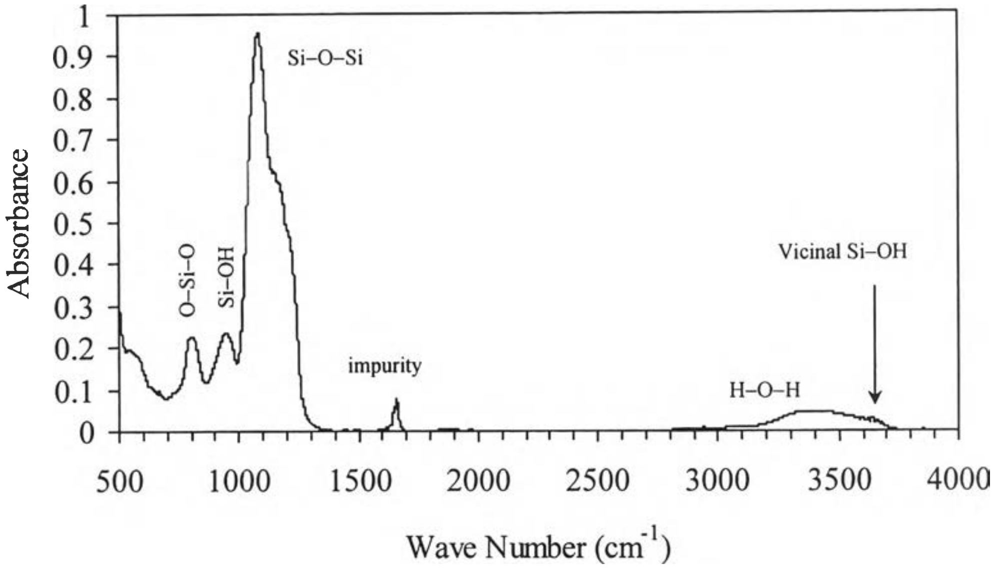

Figure 4.13 FTIR spectra of silica gel precipitates from the experiment using 4M HCl at 25°C.

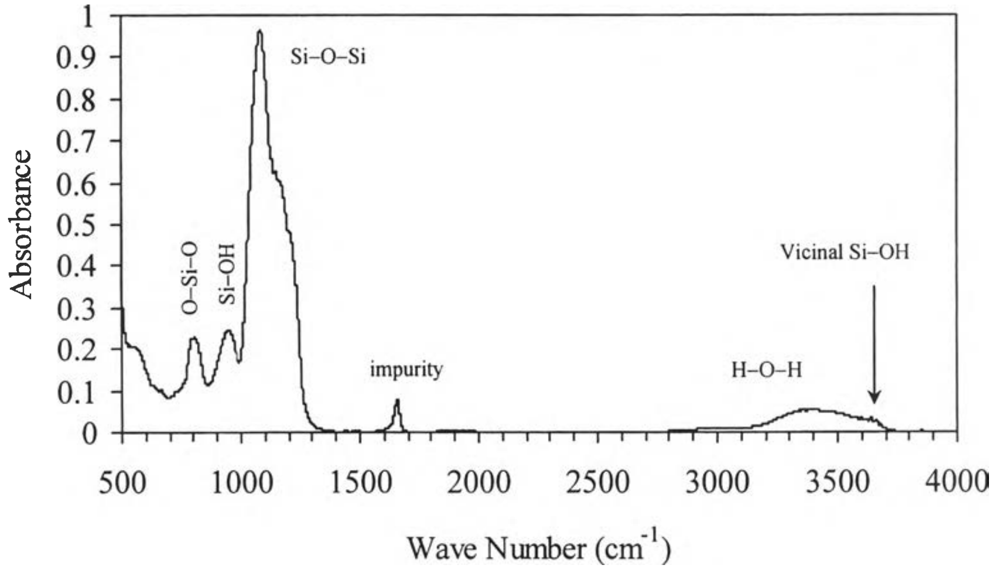

Figure 4.14 FTIR spectra of silica gel precipitates from the experiment using 7M HCl at 25°C.

Table 4.3 shows absorption peaks of some functional groups, which are used as references. The IR spectra indicate that there is a sharp absorption peak around 1080 cm^{-1}, which is the stretching vibration of the Si–O– Si bonds without non-bridging oxygen. The absorption at 960 and 800cm^{-1} indicate the Si–OH and O–Si–O stretching, respectively. In OH–stretching region between 3200 and 3800 cm^{-1}, two peaks are detected. The first peak at 3265-3645 cm^{-1} is due to absorption of water on the gel. The second peak at ~ 3650 cm^{-1} is due to very few weakly hydrogen bonded vicinal silanol. The results indicated that the silica gel precipitates from the dissolution of analcime in solutions of 4 M and 7 M HCl at 25°C are similar, and the gel precipitates are essentially pure silica gel.

Table 4.3 IR band assignments (Pouchert, 1985)

Wave number (cm^{-1})	Assignment
600	Al–O–Al Stretching
800	O–Si–O Stretching
960	Si–OH Stretching
1080	Si–O–Si Stretching
3265-3645	H–O–H Stretching
3650	Vicinal Si–OH Stretching

4.5 Determination of the Rate-Limiting Step

The rate-limiting step of the dissolution reaction of analcime with 1 M HCl solution at 25°C was investigated using the differential reactor. Flow rates ranging from 10 to 25 ml/min were studied. Table 4.4 shows the dissolution rates of aluminum from analcime using 1M HCl at different flow rates. The rate-limiting step of the dissolution can be determined by plotting the dissolution rate of aluminum versus square root of HCl flow rate as shown in Figure 4.15. The results indicated that the reaction rate of aluminum dissolution was constant with the flow rates of HCl solution in the range of 15 to 25 ml/min. Under high flow rate of HCl solution, the aluminum dissolution rate became reaction-limiting. The surface reaction rate of aluminum dissolution using 1M HCl was $3.935\text{x}10^{-5}$ mol Al/g·min, which was higher than rate of aluminum dissolution in the batch experiment.

Table 4.4 Dissolution rates of aluminum from analcime using 1 M HCl at different flow rates.

Flow rate (ml/min)	$-r_{Al}$ (mol Al/g·min)
10	$2.46\text{x}10^{-5}$
	$2.96\text{x}10^{-5}$
15	$3.92\text{x}10^{-5}$
	$3.82\text{x}10^{-5}$
20	$4.20\text{x}10^{-5}$
	$3.94\text{x}10^{-5}$
25	$3.86\text{x}10^{-5}$
	$3.88\text{x}10^{-5}$

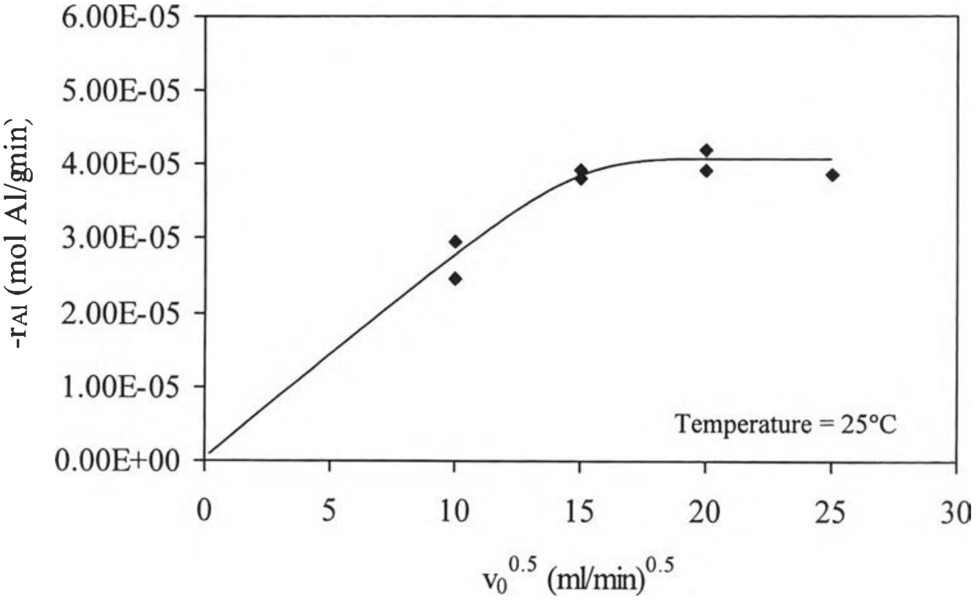

Figure 4.15 Plot of dissolution rate of aluminum from analcime versus square root of the flow rate of 1M HCl.