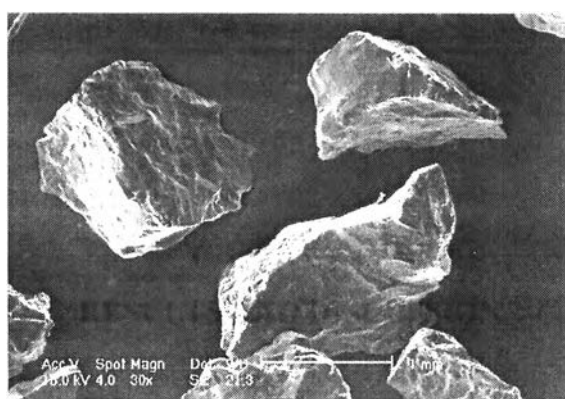


CHAPTER IV

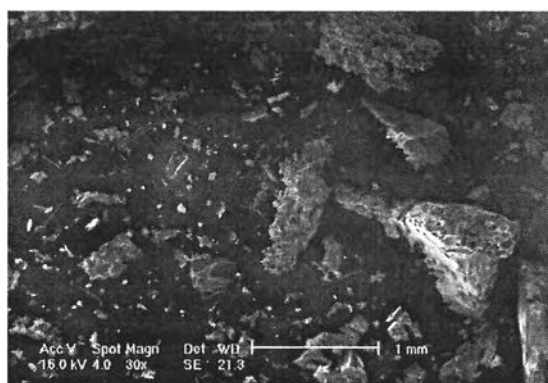
RESULTS AND DISCUSSION

4.1 The Study of the Nature of Acid Attack

The nature of acid attack was studied by performing experiments in vials on an agitator. The particles of analcime were found to break into small pieces as time progressed.



(a)



(b)

Figure 4.1 (a) Analcime in the sieve size of 0.71-1.18 mm before reaction (reaction time = 0) and (b) after reacting with 0.2M HCl (reaction time = 24 hr).

Figure 4.1 showed the picture of analcime particles before and after reacting with 0.2M HCl for 24 hr. It was obviously seen that analcime particles broke into small pieces after the dissolution reaction occurred.

The breakage of particles can also be seen from the shift of size distribution. Figure 4.2 illustrates the change of size distribution of analcime particle as the reaction proceeded. The amount of the large particles was found to decrease as the reaction time increase while the amount of small particles increases. The average particle size remained quite constant from the beginning until at time around 0.15 hr before decreased dramatically at time about 0.25 hr. The critical breaking time is defined as the time when the amount of the large particles decrease dramatically or when the average size of particles decreases dramatically. In this experiment, the critical breaking time is 0.25 hr.

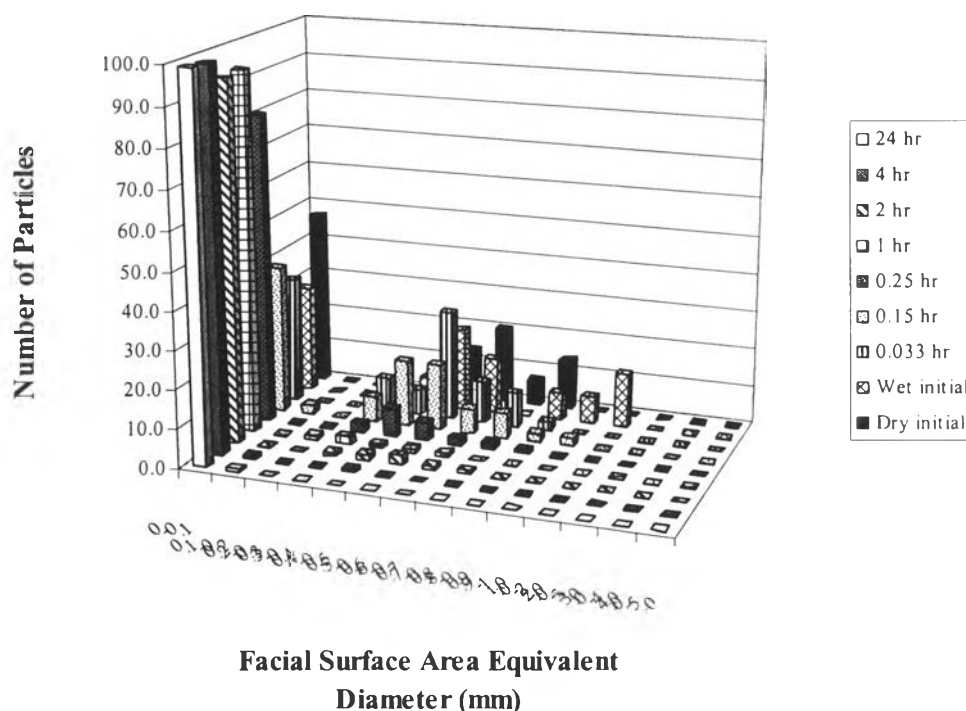


Figure 4.2 The change of size distribution as a function of time (sieve size 0.71-1.18 mm, 0.2M HCl, 25°C).

This observed phenomenon indicates that HCl or hydrogen ion may have diffused through the pores on the surface of analcime into its internal surface where

dissolution reaction occurred and then led to breaking apart of the particles. This hypothesis is as shown in Figure 4.3.

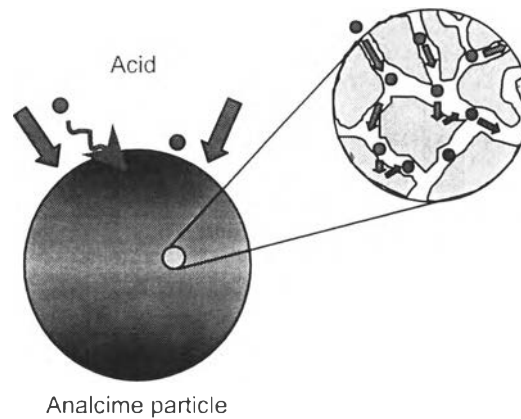


Figure 4.3 The diagram shows the hypothesis of the mechanism of breaking of analcime particles.

4.1.1 Effect of Water and Filtration to Analcime Particles

Figures 4.4 and 4.5 show the change of the size of analcime particle after mixing with deionized water and being filtered out immediately and after 24 hr. SEM pictures were used to observe the change in both the size distribution and the surface of analcime particle.

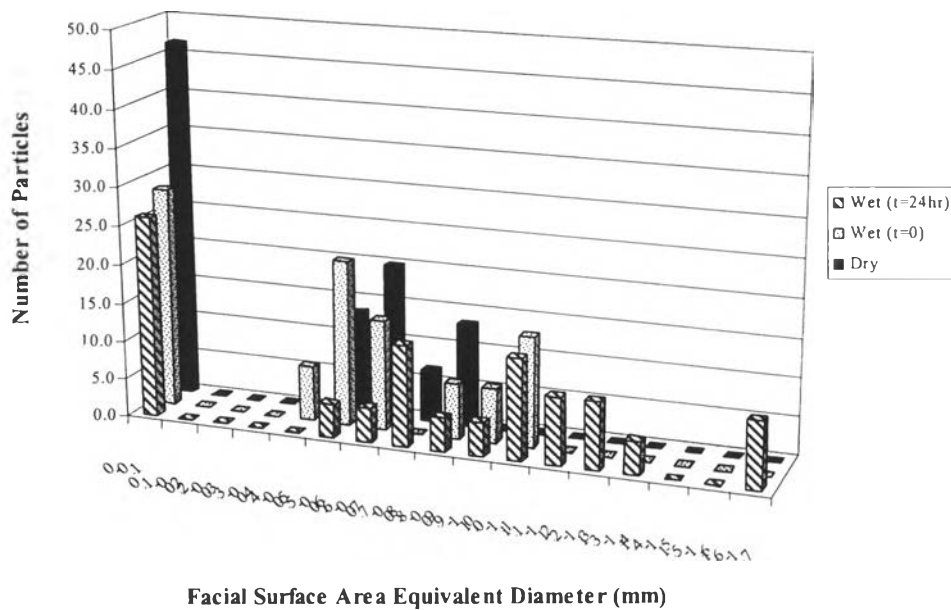


Figure 4.4 The difference in size distribution between dry analcime and analcime left in deionized water for 0 hr and 24 hr (sieve size 0.71-1.18 mm).

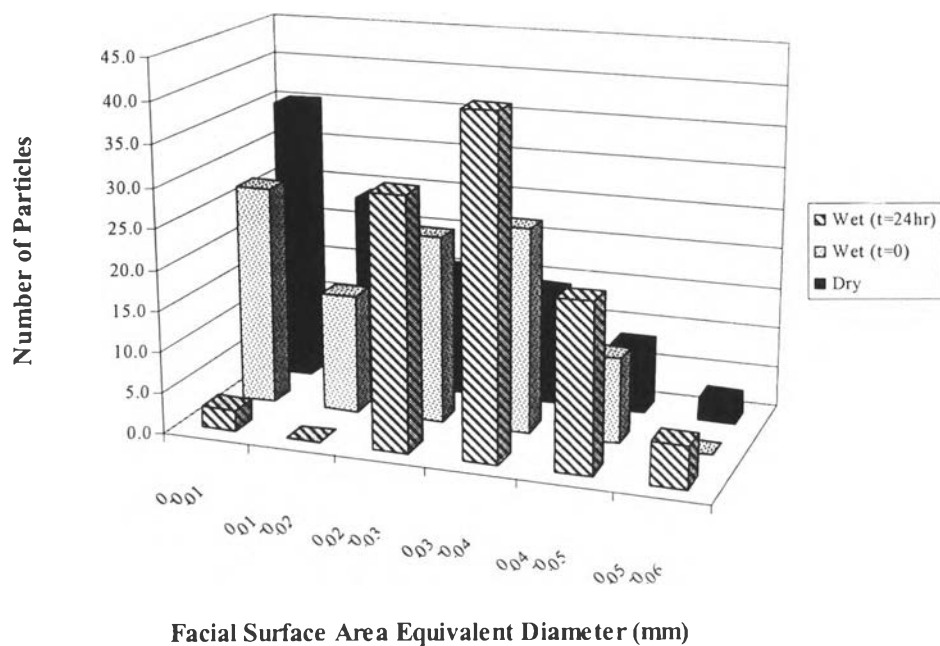


Figure 4.5 The difference in size distribution between dry analcime and analcime left in deionized water for 24 hr (sieve size 0.045-0.075 mm).

Figure 4.6 shows the surface of analcime particles (sieve size 0.045-0.075 mm) before and after the mixing with deionized water and the filtration. It was found that the ratio of Si: Al: Na does not change significantly. The pictures from SEM also show that there is no change in surface of analcime particle. The change that can be observed is the slightly decrease in the amount of very fine particles which may be explained by the fact that some small particles may be washed out by filtration.

However, it may be possible that water has played the role in enhancing the dissolution reaction by its hydroxyl ion as the reaction proceeded. After contact with water for a period of time, the analcime particle may become swell and thus lead to the structure that may be easier to be attack by acid.

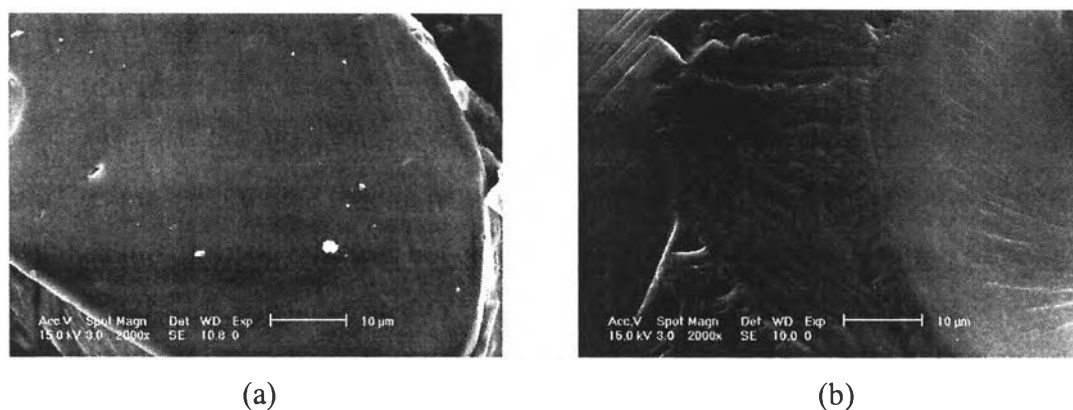


Figure 4.6 The surface of analcime particles (a) before (molar ratio Si: Al: Na equal 2.85: 1.33: 1.00) and (b) after (molar ratio Si: Al: Na equal 2.28: 1.04: 1.00) the mixing with deionized water and the filtration (sieve size 0.045-0.075 mm).

4.1.2 The Effect of the Particle Size on the Breaking of Particles

The effect of the particle size was studied by performing experiments in 0.1M HCl. The results are illustrated in Figures 4.7 and 4.8. Two different sizes of analcime; 0.045-0.075 mm and 0.71-1.18 mm, were studied. The critical breaking time was found to increase as the initial size of analcime particles increases (the critical breaking time was found to be 0.5 hr and 1 hr for 0.045-0.075 mm and 0.71-

1.18 mm, respectively). This is because in large particles, acid needs longer time to diffuse through the pores or channels to dissolve the internal structure. Moreover, the small particles have higher reactive surface area also enhances the dissolution reaction in the internal structure of analcime particles. However, the critical breaking time can be indicated in the case of the large particles more easily than in small particles that is because in large particles, the number of particles shows the great change while there is only a slightly change observed in small particles. This phenomenon can be explained by the high surface area of small particles which leads to the dissolution of the external surface at a very high rate. Therefore, the particles shrink at a very fast rate. Since the initial size of 0.045-0.075 mm is so small, the size of the particles resulted from the shrinking and the size of the particles from the breaking of the particles are very close. Therefore, the critical breaking time is difficult to be observed. It can be seen that the fluctuation exists in both initial sizes of analcime especially in 0.045-0.075 mm analcime. This may be caused by the dissolution of fine particles from the breaking of particles. Since the fine particles are very small, the dissolution reaction occurred rapidly, therefore, leads to rapid decrease in the number of particles.

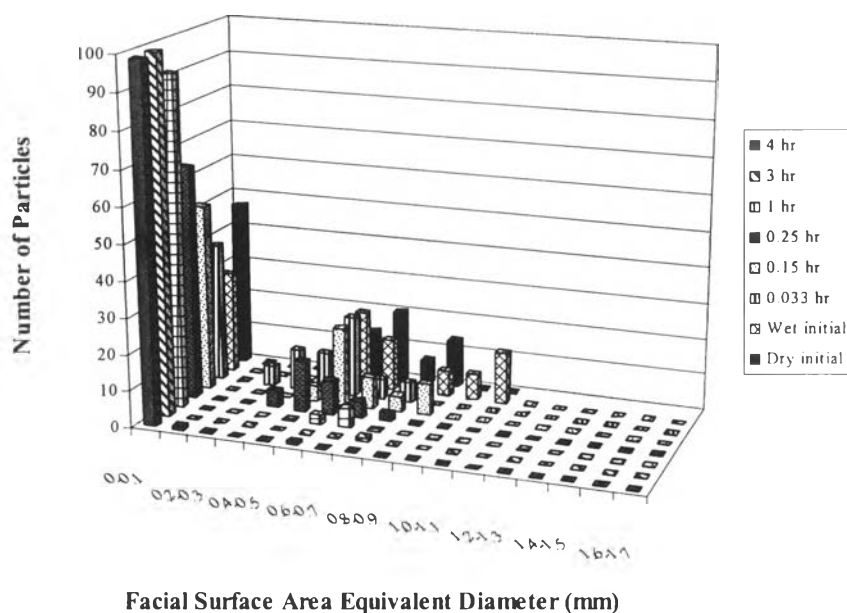


Figure 4.7 The change in particle size analcime (sieve size 0.71-1.18 mm, 0.1M HCl, 25°C).

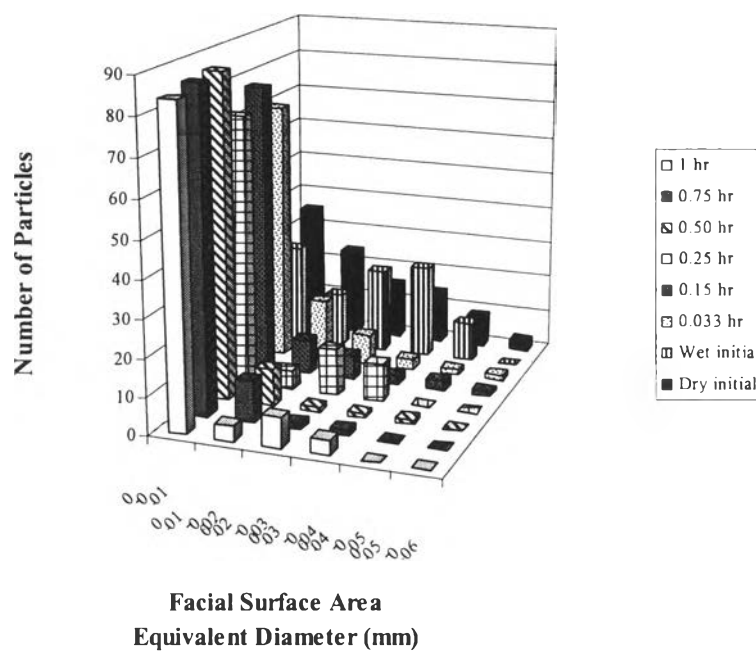


Figure 4.8 The change in particle size analcime (sieve size 0.045-0.075 mm, 0.1M HCl, 25°C).

4.1.3 The Effect of Acid Type on the Breaking of Particles

The effect of acid type was studied by carrying the experiments with two different types of acid; hydrochloric acid and citric acid. The initial concentrations of acid were 0.2M (pH 1.22) for hydrochloric and 3M for citric acid (pH 1.29) in order to obtain the same pH. Figures 4.9 and 4.10 illustrate the change in size distribution as a function of time for analcime in 3M citric acid and 0.2M HCl, respectively. The critical breaking time was found to be 0.25 hr for both HCl and citric acid. It can be seen that there is no significant difference between hydrochloric and citric acid in the term of the critical breaking time which may be because there is only hydrogen diffused into the internal structure of analcime instead of acid molecule. However, there may be difference in the size distribution at longer time since citric acid is a weak acid so the particle can break into pieces before it shrink. On the other hand, hydrochloric which is a strong acid can dissolve the particle very fast so that the particle shrinks and becomes small particle before it breaks apart.

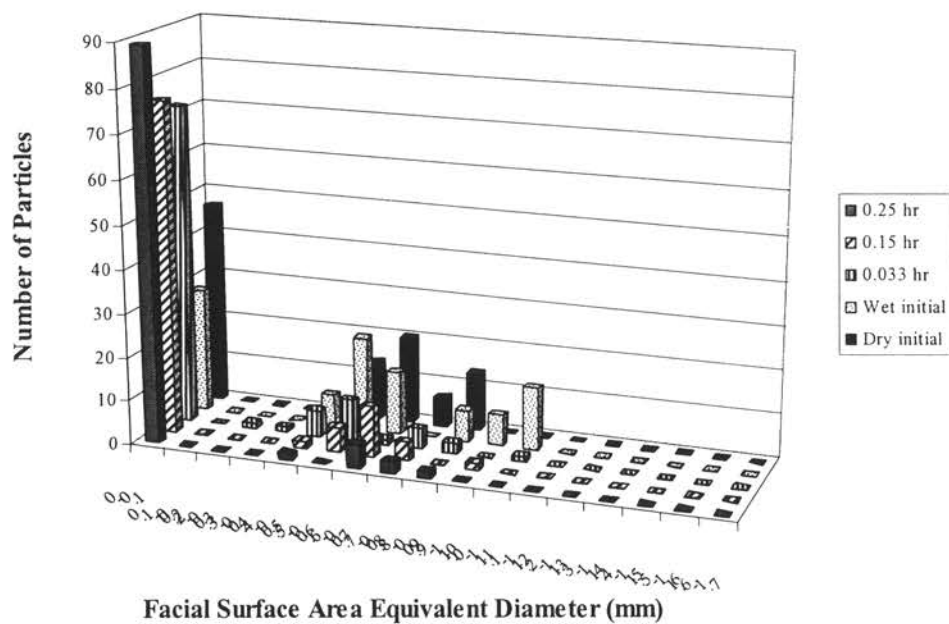


Figure 4.9 The change in size distribution as the time pass (sieve size 0.71-1.18 mm, 3M citric acid, 25°C).

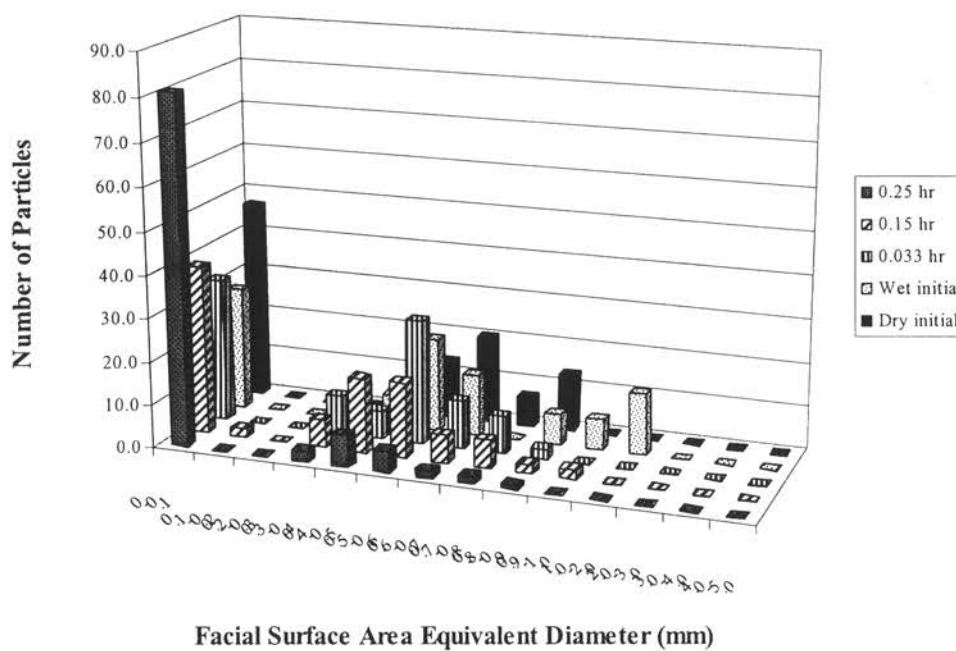


Figure 4.10 The change in size distribution as the time pass (sieve size 0.71-1.18 mm, 0.2M HCl, 25°C).

4.1.4 The Effect of Acid Concentration on the Breaking of Particles

The effect of acid initial concentration was studied by using two different concentrations of acid; 0.1M and 0.2M HCl. The size distribution of particles as a function of time for 0.1M and 0.2M are shown in Figures 4.7 and 4.10, respectively. The critical breaking time is 1 hr for 0.1M HCl and 0.25 hr for 0.2M HCl. It is apparent that at higher acid concentration, the breaking of particles occurs faster than at lower concentration. This phenomenon can be explained by the fact that higher concentration leads to higher concentration gradient of hydrogen ion which causes more diffusion and dissolution in the internal structure of analcime particles.

4.1.5 The Effect of Surface Composition on the Breaking of Particles

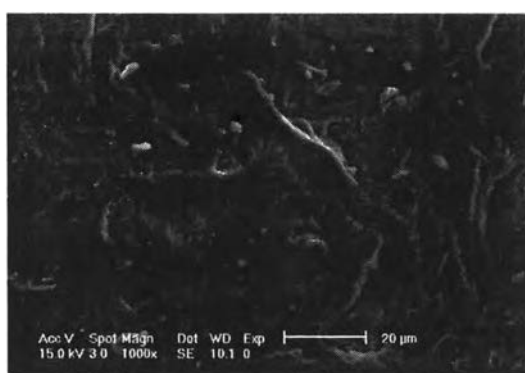
The surface of the dissolved analcime particles was found to be different even in the same batch with same acid, initial size of particles and reaction time. This phenomenon may occur by the difference in the surface composition caused by the different plane of crystal structure. Since analcime consists of tetrahedral of Al and Si, the Al which needs Na ion in order to balance its charge and make the structure stable. On this type of site, analcime may have less strength and then may be attacked with acid more easily than the site where Si is sitting instead of Al, thus leading to more surface dissolved.

4.1.6 The Change in Surface Composition

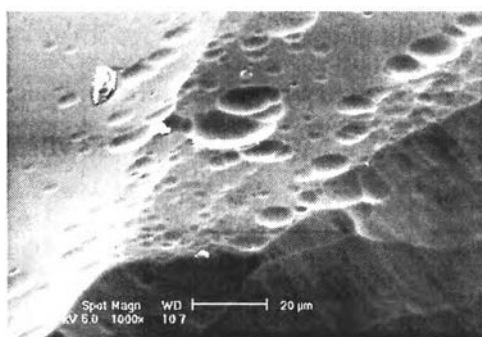
The analcime particles remained after the dissolution reaction was analyzed by Energy Dispersive X-ray Spectroscopy (EDX). The surface composition was found to be different in different area. Figure 4.11 shows the pictures of surface before and after the reaction with HCl along with their surface compositions.

It was found that after the reaction occurred, the molar ratio of Si: Al: Na on the surface of analcime particle increase. The dissolved surface was also found to be attacked at different patterns. The ratio of Si to Al and Na is higher in the case of rough surface (Figure 4.11c) than the smoother surface (Figure 4.11b). There are two

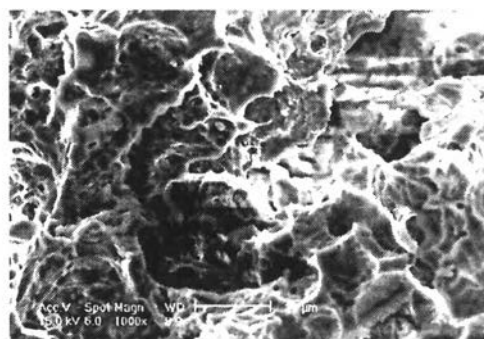
explanations of this phenomenon. First, Si may precipitate and deposit on the surface of analcime particles. Or Al and Na may be leached out from the analcime structure since Na has the ability of ion exchange. It can also be observed that the ratio of Al to Na for the rough surface is higher than the other. The reason may be that Na was leached at the faster rate than Al. So Na may be removed first following by Al and finally Si.



(a)



(b)



(c)

Figure 4.11 Different surface of analcime particles (sieve size 0.71-1.18 mm) (a) before the reaction (surface composition of molar ratio Si: Al: Na equal 2.52: 1.18: 1.00) and after reacting with 0.2M hydrochloric acid for 24 hr at 25°C with surface composition of molar ratio Si: Al: Na equal (b) 2.96: 1.35: 1.00 and (c) 4.00: 1.52: 1.00.

4.1.7 Reaction Order of the Dissolution Reaction

Figure 4.12 shows the correlation between the initial rate ($-r_{i,0}'$, mole/g/hr) and the concentration of hydrochloric acid. The initial rate was calculated from the correlation between the concentration of each dissolved element and the reaction time which was obtained from each vial. The reaction order with respect to the concentration of hydrochloric acid was found to be approximately one with respect to the hydrochloric acid concentration.

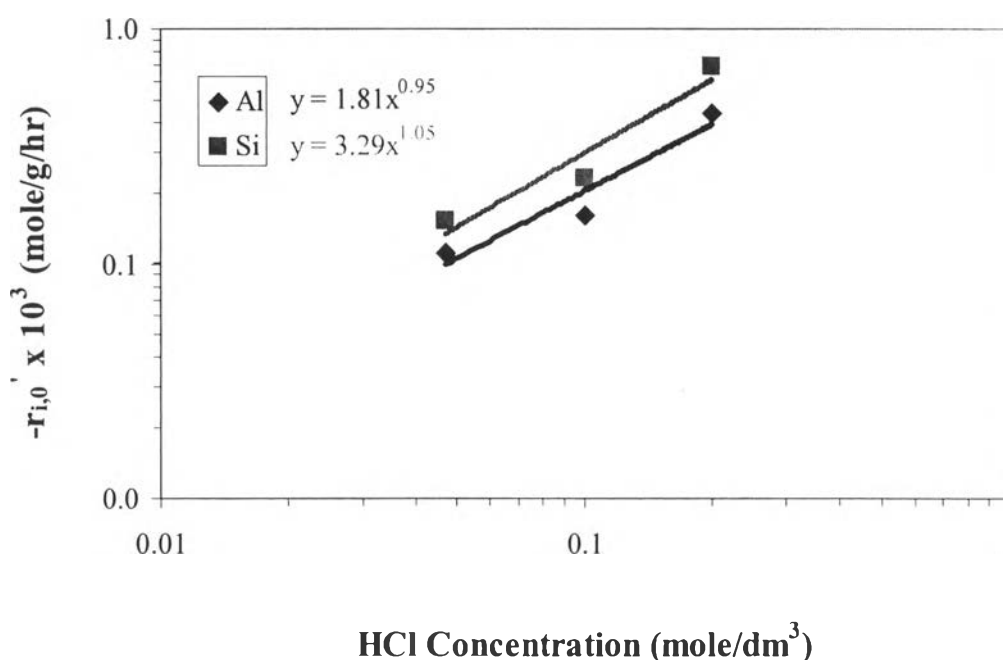


Figure 4.12 Initial rate of dissolution reaction as a function of acid concentration (sieve size 0.71-1.18 mm, 25°C).

4.2 Study of the Dissolution Kinetics

The experiment was carried out in the 1000 ml flask reactor. Analcime in the size of 0.71-1.18 mm was placed into citric acid solution at room temperature (25°C) with agitation speed of 250 rpm. The facial surface area equivalent diameter and the specific surface area of analcime from SEM pictures were found to be 0.6875 mm and 3.97×10^6 mm²/g, respectively. The initial rates of dissolution of each

element were calculated from the slopes of linear fitting to the initial concentration of dissolved elements versus time. The concentration of each element as a function of time is shown in Figure 4.13.

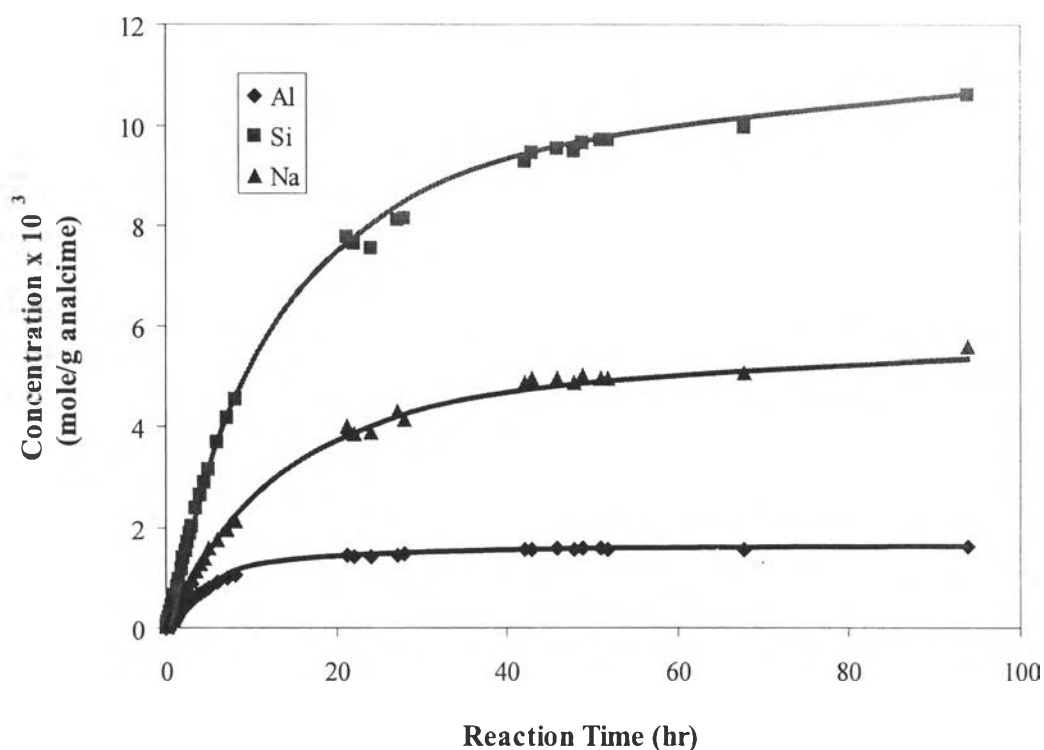


Figure 4.13 Concentration of Al, Si and Na per initial weight of analcime as a function of time (sieve size 0.71-1.18 mm, 0.1M citric acid, 25°C).

It can be seen from Figure 4.13 that the dissolution of Si is faster than Na and the dissolution of Na is faster than Al. The initial rates were found to be 0.53×10^{-3} , 0.20×10^{-3} and 0.23×10^{-3} mole/g/hr for Si, Al and Na, respectively (calculated from Figure 4.13). The ratio of the initial rates of Si: Al: Na was found to be 2.69: 1.00: 1.17. The ratio of the final concentration (at time approximately 95 hr) of Si: Al: Na was found to be 6.65: 1.00: 3.49.

This phenomenon may be explained by the fact that Al precipitated as the citrate of aluminum in the system, or Na and Si may be leached out from the structure of analcime.

4.2.1 Effect of Initial Analcime Particle Size on the Dissolution Rate

The effect of mass transfer on the dissolution reaction was studied by carrying experiments at various particle sizes ranges of analcime. In this study, analcime was sieved into three different sizes, 0.045-0.075 mm, 0.150-0.180 mm, and 0.212-0.300 mm to be used in the experiments. All the experiments were performed at room temperature with 0.1 M citric acid. The ratios of analcime to acid were fixed at 1 gram of analcime to 150 ml of acid. All experiments were carried out at a fixed stirring speed (250 rpm). Sample solution was analyzed by pH meter and AAS for the concentrations of hydrogen ions, Al, Si and Na while the solid obtained from filtration was analyzed by SEM and EDX to observe the surface and determine the composition.

Figures 4.14 shows the concentration of Al for different initial sizes of analcime particles as a function of time on the basis of initial weight.

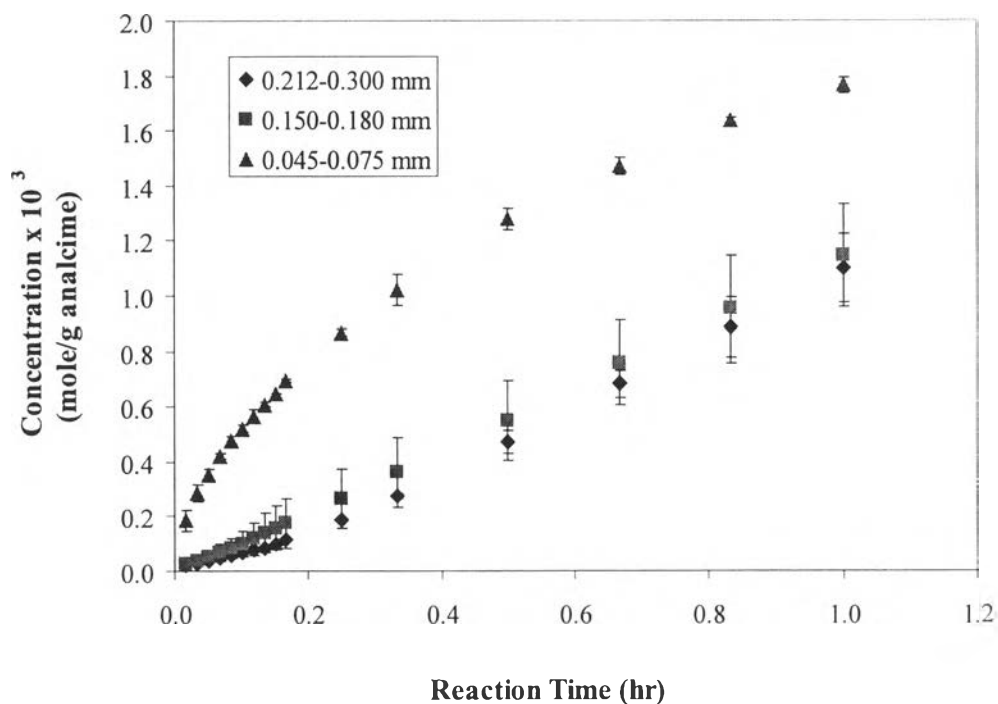


Figure 4.14 Al concentration per initial weight of analcime as a function of time for different initial sizes (demonstrated by the sieve size) of analcime particles (0.1M citric acid, 250 rpm, 25°C).

From Figure 4.14, the initial rate of Al per initial weight of analcime was found to increase as the initial size of analcime particles decrease. This may be due to the increase in reactive surface area when decrease the particle size.

4.2.2 Effect of External Diffusion on the Contribution of Dissolution

Figure 4.15 shows the concentration of Al for different initial sizes of analcime particles as a function of time on the basis of specific surface area (calculated from SEM pictures) of analcime particles. The initial rate of Al was found to change as the size of the particle change.

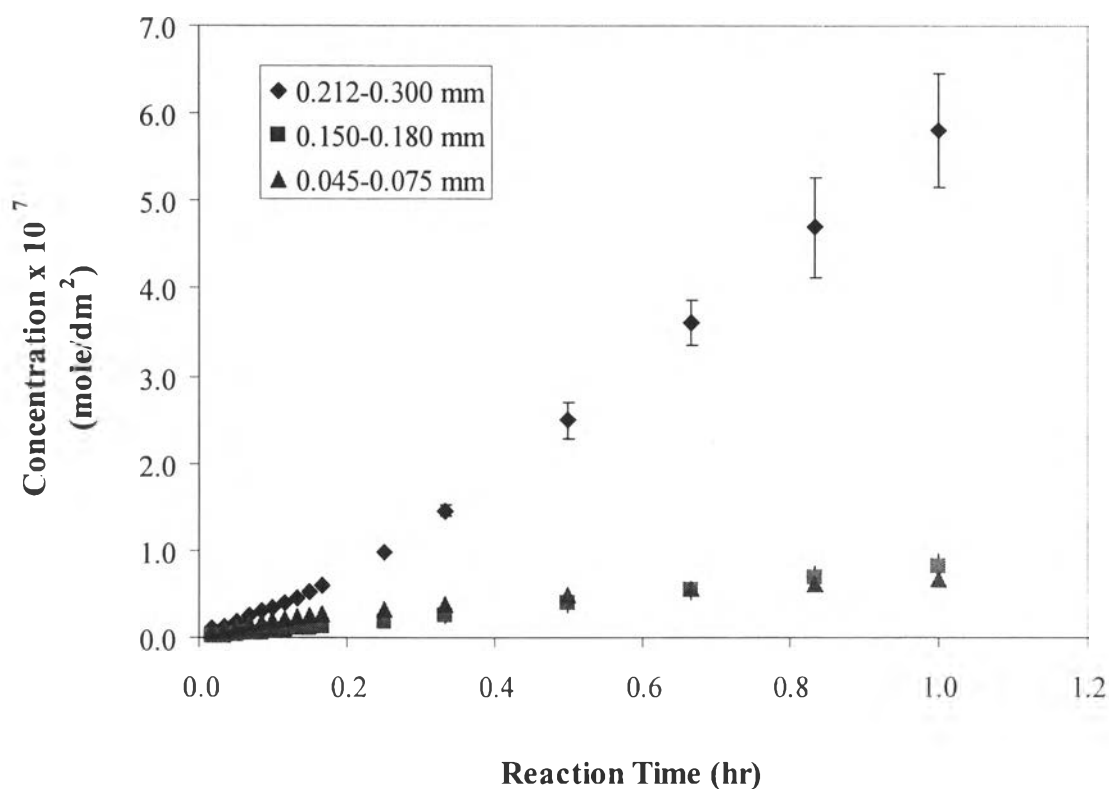


Figure 4.15 Al concentration per specific surface area of analcime as a function of time for different initial sizes (demonstrated by the sieve size) of analcime particles (0.1M citric acid, 250 rpm, 25 °C).

Table 4.1 summarizes the value of the facial surface area equivalent diameter of analcime particles, the specific surface area, and the initial rate in both basis.

Table 4.1 Initial rate per external surface area

Initial size (mm)	Average facial surface area equivalent diameter (mm)	External specific surface area $\times 10^{-4}$ (dm^2/g)	Initial rate weight basis $\times 10^3$ (mole/g/hr)	Initial rate area basis $\times 10^7$ (mole/ dm^2/hr)
0.045-0.075	0.020	2.63	3.34	1.27
0.150-0.180	0.085	1.39	1.00	0.72
0.212-0.300	0.169	0.19	0.60	3.17

From Table 4.1, although it appears that there is much less difference in the values of the initial rate per specific surface area than the rate per weight basis, but it is clear that there is still noticeable difference between the rates per area from the three sizes. This result reveals that the external diffusion does not dominate the contribution of the dissolution reaction. That is the internal diffusion may have the influence on the dissolution as much as or more than the external diffusion does.