CHAPTER III
EXPERIMENTAL

3.1 Materials

Analcime is a natural zeolite. Its properties are described in Table 3.1.

Table 3.1 Properties of analcime (Material Safety Data Sheet acc. to OSHA and ANSI, 2000)

Chemical formula	$Na_2O.Al_2O_3.4SiO_4.2H_2O$
Color	Colorless to white
Odor	Odorless
Crystallography	Cubic, Ia3d
Diameter	0.045-1.20 mm
Specific surface area (BET)	5×10^5 mm^2/g
Specific gravity	2.22-2.29
Pore size	1.6 x 4.2 Å

Analcime was obtained from Sigma-Aldrich, Inc. Two different acids, hydrochloric and citric acid were used as acidizing agent in this study. Hydrochloric was a representative of an inorganic acid while citric acid was a representative of an organic acid. Hydrochloric solutions were prepared by dilution of desired amount of laboratory grade acid supplied by Fisher Scientific, Inc. in deionized water. Citric acid solutions were prepared from citric acid in the solid form mixed with deionized water. Solid citric acid was obtained from Sigma-Aldrich, Inc. Aluminum, silicon and sodium reference standard solutions for Atomic Absorption Spectrophotometer (AAS) were supplied by Fisher Scientific, Inc.

3.2 Pretreatment of Analcime

The raw analcime was crushed and sieved into four desirable size ranges, 0.71-1.18 mm, 0.212-0.300 mm, 0.150-0.180 mm, and 0.045-0.075 mm. Crushed analcime was then dispersed in deionized water and cleaned in a sonicator bath for 20 minutes to remove the fine particles. After rinsing with deionized water, the settled analcime was left in an oven at approximately 50°C over night and then kept in a desicator.

3.3 Characterization of Analcime

The analcime was examined its elemental composition by using Atomic Absorption Spectrophotometer (AAS) and Energy Dispersive X-ray Spectroscopy (EDX). The amounts of Si, Al and Na in analcime were determined in term of the molar ratios. A known amount of analcime was first dissolved in 4 wt% hydrofluoric acid and the solution was then analyzed by AAS (Perkin Elemer 3100 Atomic Absorption Spectrophotometer). EDX (Philips XL30FEG) was used to directly verify the composition of analcime.

Table 3.2 Analcime elemental analysis

Sample	Mol%				%X
	Si	Al	Na	Others (Ca, Fe, Mg)	
1	53.60	26.90	19.00	0.5	97.0
2	49.90	28.20	21.40	0.5	100.0
3	56.80	27.10	15.20	0.9	99.9
4	59.70	27.40	12.70	0.2	100.0
Average	55.0	27.4	17.1	0.5	
Std.	4.3	1.3	5.0	0.2	
Molar ratio	4.01	2.00	1.24	-	
Std.	0.35	0.10	0.27	-	

The ratio of Si to Al was found to be approximately 2 to 1 which agree with the theoretical molecular formula (Murphy et. al., 1996). However, the ratio of Al to Na was found to vary in the range of 1 to 1 and 2 to 1 which does not follow the theory. This may be either because of the impurity present or leaching of some of Na ions from the structure of analcime.

3.4 The Study on the Nature of Acid Attack

The nature of acid attack was studied by carrying experiments in 20 ml vials. Each vial contained 0.1 g of analcime with 10 ml of acid. Two different types of acids were used, citric acid and HCl. After adding analcime into the acid solution, vials were then placed in the shaker. The reaction in each vial was stopped by vacuum filtration (within approximately 1 min) with filter paper (0.22 μm pore size) at different time intervals. The morphology of the analcime particles remained on the filter paper was then examined using a Philips XL 30 FEG Scanning Electron Microscope (SEM) and the surface composition was determined with Energy Dispersive X-ray Spectroscopy (EDX). The number of particles was estimated by counting by hand and the particle size was measured using statistical imaging software (ImageJ). Atomic absorption spectrophotometer and a pH meter were employed for determining the concentration of Al, Si, Na and hydrogen ions in the filtrate.

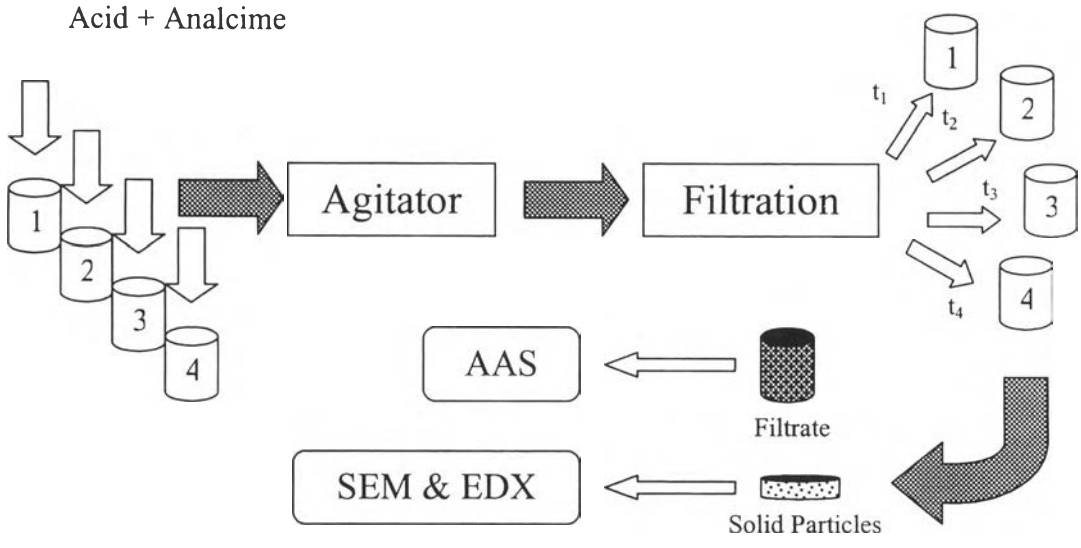

Figure 3.1 Experimental procedures for the study of the nature of acid attack.

3.5 The Study on the Reaction Kinetics

Initial rate experiments were carried out in a slurry reactor shown schematically in Figure 3.1 to determine the dissolution rate. The reactor was a 1000 ml glass flask with a magnetic stirrer for agitation. The stirring rate used was 250 rpm. All experiments were carried out at room temperature (25°C). In each experiment, 2 g of analcime was mixed with 500 ml of acid solution. For the particle size experiments, 1 g of analcime was dissolved in 150 ml of acid solution. All of the experiments in this part were performed using citric acid.

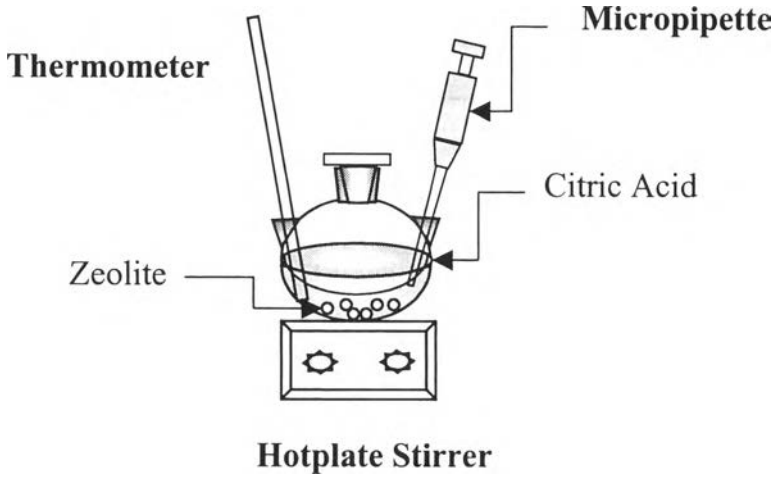

Figure 3.2 Slurry reactor for dissolution reaction study.