CHAPTER III
EXPERIMENTAL

3.1 Materials

Zeolite used in this study was analcime. Analcime, obtained from Alfa Aesar (a Johnson Matthey Company), is a naturally occurring mineral. 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	: $Na_2O{\cdot}Al_2O_3{\cdot}4SiO_4{\cdot}2H_2O$
Color	: whitish
Form	: chunks
Odor	: odorless
Density (20°C)	: 2.22-2.29 g/cm^3

Two acids, hydrochloric acid and hydrofluoric acid were used as acidizing agent in this study. Hydrochloric acid (laboratory grade), supplied by Fisher Scientific, was used throughout this study. Hydrochloric solutions were prepared by dilution of desired amount of commercial acid in deionized water. Hydrofluoric acid (laboratory grade), obtained from Aldrich, was used to verify the analcime purity and amorphous silica gel precipitates. Aluminum and silicon reference standard solutions for atomic absorption spectroscopy (AAS) were supplied by Fisher Scientific.

3.2 Pretreatment of Analcime

The raw analcime was sieved to classify the grain into a size range of 0.707-1.19 mm. Then, it was dispersed in deionized water for 1-10 minutes to remove the

fine particles. The settled analcime particles were dried in an oven and, then, kept in a desiccator. This procedure was used to ensure that the particle size and surface area of the analcime particles were uniform.

3.3 Verification of Analcime Purity by Elemental Analysis

The purity of analcime used in these experiments was chemically examined by determining Si/Al/Na mole ratios in the lattice. The molar ratio was determined by using both atomic absorption apectroscopy (AAS) and energy dispersive X-ray spectroscopy (EDX). The molar ratio was determined by dissolving a known amount of sample analcime in hydrofluoric acid solution. The dissolved lattice components were analyzed by using an atomic absorption spectroscopy (Varian Spectro AA, 300). Moreover, an energy dispersive X-ray spectroscopy (Philips XL30FEG) was used to directly verify the composition of the analcime sample.

3.4 Analcime Dissolution Study

The dissolution rates of analcime were measured by initial rate experiments which were carried out in a slurry batch reactor as shown in Figure 3.1. The details of this experimental proceure were described in a previous study (Kline and Fogler, 1980). The reactor was a 500 ml glass flask that used a magnetic stirrer for agitation. The stirring rate used in each experiment was 1100 rpm. In each experiment, 2 g of analcime (particle size 0.707-1.19 mm) were placed with 300 milliliters of (0.1-7 mol/l) hydrochloric acid solution in the slurry reactor. The experiments were carried out at two temperatures of 25°C and 45°C. The samples were withdrawn by micropipettes at short time intervals and, then, filtered through the membrane filters (pore size 0.22 micron, 25 mm diameter). Filtration of the suspended particles was used to stop the dissolution reaction, so the filtrate samples represented dissolved mineral as a function of time.

The progress of the dissolution reaction was monitored by analyzing the filtrate samples for dissolved aluminum and silicon as a function of time using atomic absorption spectroscopy.

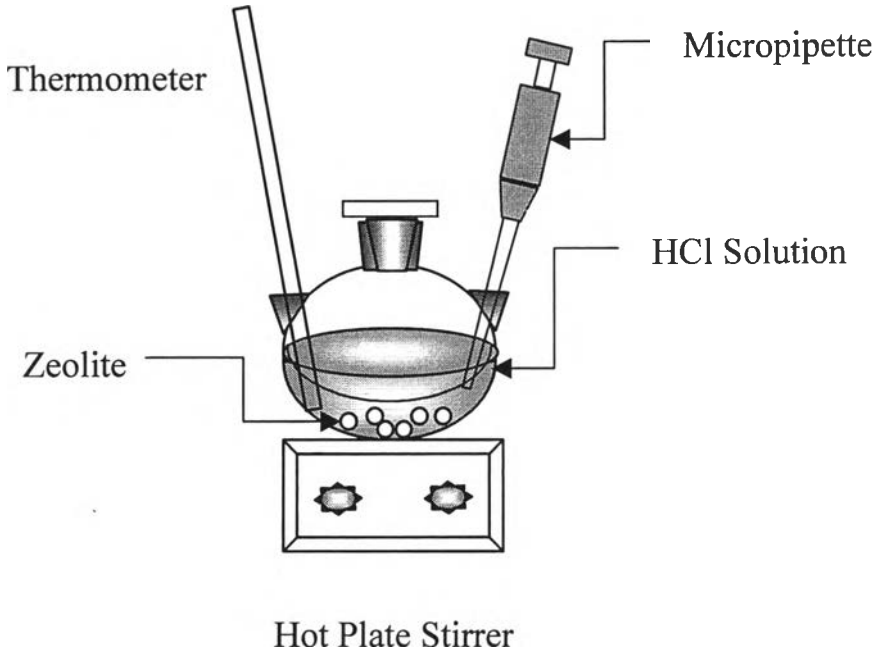

Figure 3.1 The slurry reactor.

3.5 Analysis of Leaching Reaction

The leaching of aluminum in analcime by hydrochloric acid (7M) was investigated by using a differential reactor as shown in Figure 3.2. A syringe pump was used to inject the hydrochloric acid solution through the differential reactor to dissolve the analcime particles (particle size 0.707-1.19 mm) at a fixed flow rate. All experiments were carried out at room temperature (25°C). In each experiment, 0.2 grams of analcime was first placed uniformly between two Millipore hydrochloric type HVPE membranes (0.45 μm pore size, 25 mm diameter), which were sealed by a Teflon O-ring mounted inside the differential reactor as shown in Figure 3.3. The hydrochloric acid solution dissolved analcime as it flowed through the reactor to a 1/6″ ID Teflon tube, which collected effluent sample at different times in glass vials using a collector. The effluent samples were analyzed for the concentrations of aluminum and silicon. The particles left in differential reactor were analyzed by energy dispersive X-ray spectroscopy to determine the chemical compositions on the surfaces.

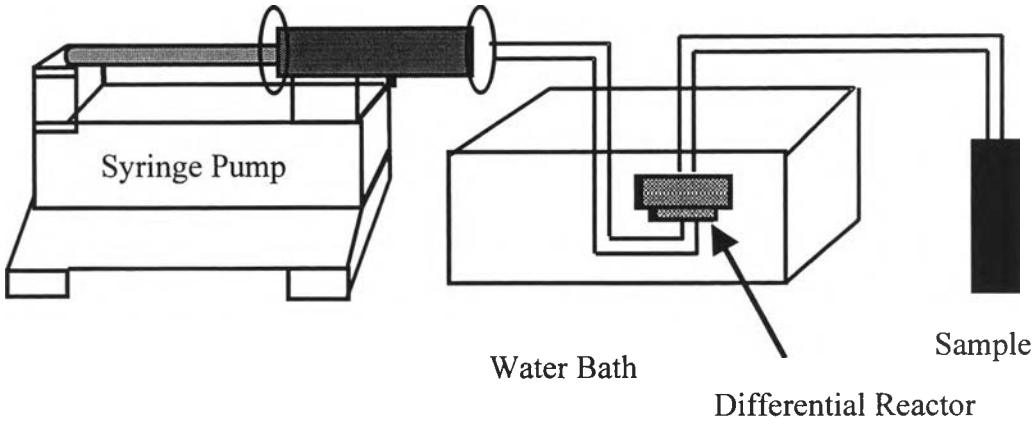

Figure 3.2 Schematic illustration of the experimental set up for the dissolution study.

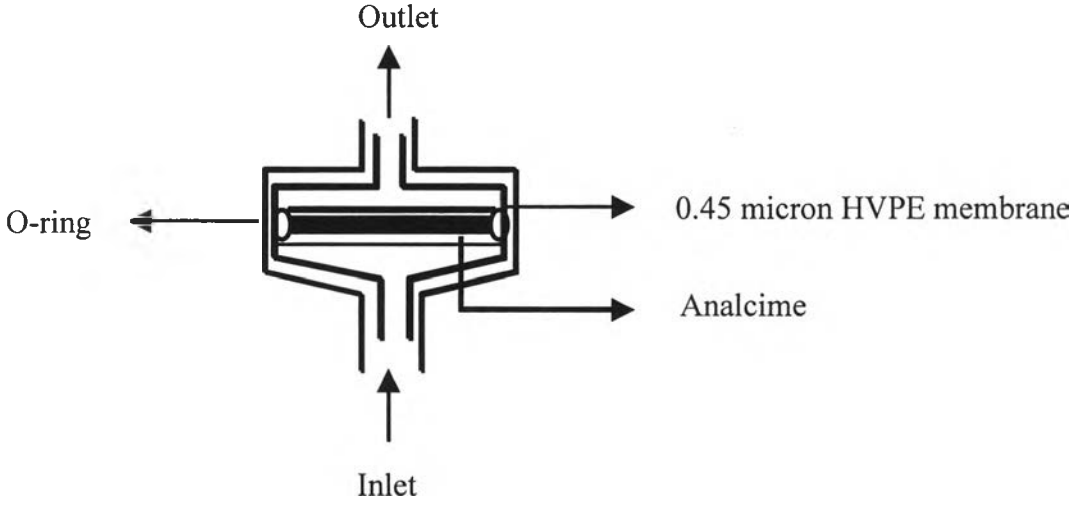

Figure 3.3 The enlarged view of the differential reactor.

3.6 Characterization of Silica Gel Precipitates

Atomic absorption spectroscopy and electron dispersive X-ray spectroscopy were used to analyze the chemical compositions of white pasty gel precipitates from dissolution. Fourier transform infrared spectroscopy (FTIR) was used to identify the functional groups of the precipitated gel.

3.7 Determination of Analcime Chemical Composition

The chemical composition of analcime was determined using atomic absorption spectroscopy (AAS) and energy dispersive X-ray spectroscopy (EDX).

3.7.1 EDX

Energy dispersive X-ray spectroscopy was used to verify analcime purity. The EDX spectrum of analcime is shown in Figure 3.4. This spectrum illustrates the absorption peak of aluminum, silicon, sodium and oxygen elements. There are no other elements appearing on the spectrum. The composition of elements in analcime sample is shown in Table 3.2. The EDX result shows that the mole ratio of Al: Si: Na equal to 1: 2.1: 0.7.

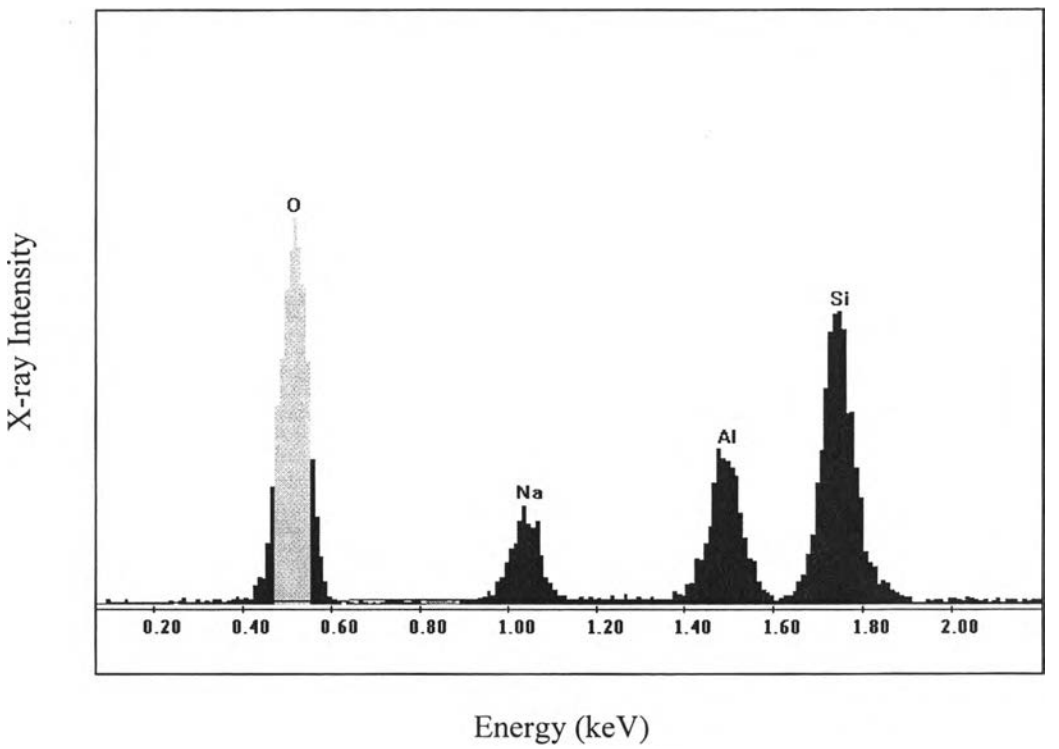

Figure 3.4 EDX analysis of analcime.

Table 3.2 Composition of elements in analcime sample

Element	wt%	mol%
O	43.96	56.87
Na	8.5	7.66
Al	14.73	11.30
Si	32.81	24.17
Total	100	100

3.7.2 AAS

The molar ratio of Si/Al/Na was determined from atomic absorption spectroscopy. A sample of analcime 0.3004 g was dissolved in 100 ml of 3.84% hydrofluoric acid. The results shows that the mole ratio of Al: Si: Na equal to 1: 2.09: 0.985.

Examination of the data from atomic absorption spectroscopy and energy dispersive X-ray spectroscopy indicates that analcime used in this study was essentially pure.