

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials

Two commercial phosphonate inhibitors were used in this study: 1-Hydroxyethylidene-1,1-diphosphonic Acid or HEDP and Aminotri(methylenephosphonic acid) or ATMP. Their properties are described in Table 3.1.

Table 3.1 Molecular structure and their properties of two used phosphonates.

<div style="text-align: center;"> </div> <p>Molecule weight: 206            Color: colorless to pale yellow in solution            Specific Gravity in Solution (20/15°C): 1.4            Acidity constants in 0.5 M tetramethylammonium chloride at 298 K:  <math>\text{HEDP} \leftrightarrow \text{HEDP}^- + \text{H}^+ \quad \text{pK}_1 &lt; 2</math>  <math>\text{HEDP}^- \leftrightarrow \text{HEDP}^{2-} + \text{H}^+ \quad \text{pK}_2 = 2.54</math>  <math>\text{HEDP}^{2-} \leftrightarrow \text{HEDP}^{3-} + \text{H}^+ \quad \text{pK}_3 = 6.97</math>  <math>\text{HEDP}^{3-} \leftrightarrow \text{HEDP}^{4-} + \text{H}^+ \quad \text{pK}_4 = 11.41</math></p>	<div style="text-align: center;"> </div> <p>Molecule weight: 299            Color: colorless to pale yellow in solution            Specific Gravity in Solution (20/15°C): 1.3            Acidity constants in 1.0 M potassium nitride at 298 K:  <math>\text{pK}_1 &lt; 2 \quad \text{pK}_4 = 5.46</math>  <math>\text{pK}_2 &lt; 2 \quad \text{pK}_5 = 6.66</math>  <math>\text{pK}_3 = 4.30 \quad \text{pK}_6 = 12.3</math></p>
---	--

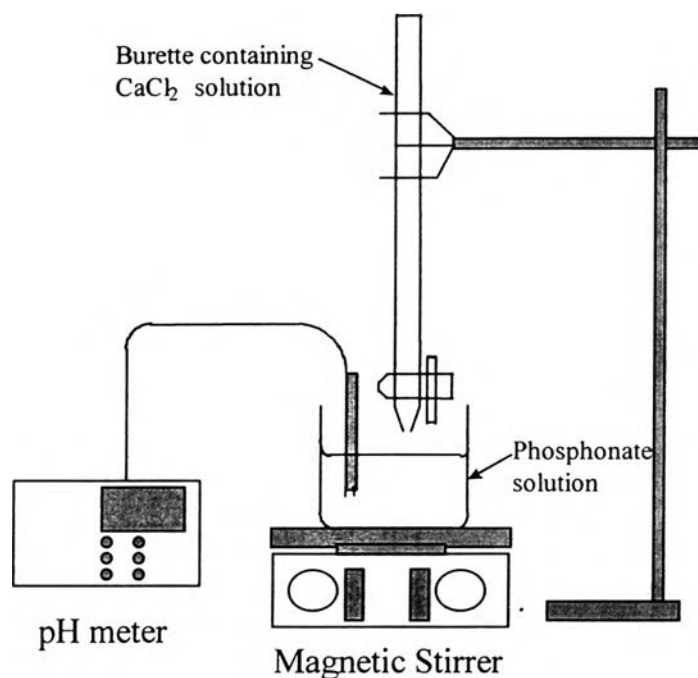


Figure 3.1 Schematic of batch synthesis apparatus.

### 3.2 Batch synthesis and characterization

The precipitates of calcium phosphonate were prepared under different conditions using a simple titration apparatus shown in Figure 3.1. All experiments were conducted at room temperature ( $\approx 25^\circ\text{C}$ ). The desired phosphonate solution was placed into a beaker which was stirred continuously using a magnetic stirrer. The fine solid potassium hydroxide and concentrated hydrochloric acid were used to adjust the pH of solution to a desired value and to maintain the pH constant during the titration. Then, calcium chloride solution was added into the phosphonate solution with 5 ml increment until the titration was completed. After the titration was completed the resulting solution was left to sit overnight to allow complete precipitation. The resulting precipitate was filtered using 0.22 micron filters membrane and the filtered precipitate was then washed with deionized water. The precipitate was finally dried in the oven at  $100^\circ\text{C}$  preparing for characterization.

The resulting precipitate was characterized by following techniques. First, the calcium to phosphonate molar ratio of the precipitate was obtained by dissolving a known amount of the precipitate in an acidic solution. Then, the solution concentrations of both species were determined. The calcium concentration were determined by using an atomic adsorption spectrophotometer while the phosphonate concentration was analyzed by oxidation and colorimetric techniques which in advance of using spectrophotometer (Hach techniques).

### 3.3 Batch dissolution

The equilibrium solubility of each precipitate was determined by using batch dissolution method. A weighted amount of precipitate was put into a beaker that contained a predetermined amount of deionized water (or desirable solution). Then, the solution was stirred continuously and a small quantity of the solution was taken periodically to determine the phosphonate concentration.

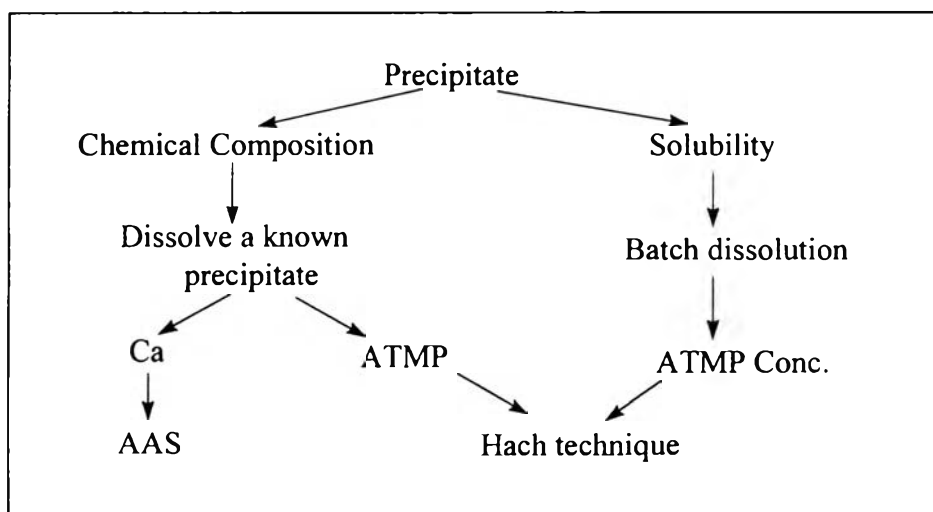


Figure 3.2 Flow chart of the characterization procedures.

### 3.4 Micromodel experiment

The experiments in micromodel were conducted in order to mimic the squeeze process. A schematic of micromodel apparatus is shown in Figure 3.3. The simulated porous medium consisted of two-dimensional glass etched micromodels (pore throat diameters ranged from 50 to 300 micron with a total pore volume of approximately  $0.15 \text{ cm}^3$ ). The micromodel experiments offer the advantage that the release of Ca-phosphonate precipitate can be visually observed.

The procedure carried out in these experiments is similar to that occurs in an actual oilfield application. The supersaturated Ca-Phosphonate solution was injected into the micromodel via a syringe pump until the micromodel was completely filled up with the solution. Next, the solution was left in the micromodel for approximately 24 hours allowing in situ precipitation to occur. After the shut-in period, the elution fluid was pumped into the micromodel to dissolve the precipitate. During this elution process, the dissolution mechanism was visually observed and recorded through the stereo-zoom microscope and super VHS video recorder while effluent samples were collected and analyzed for phosphonate concentration.

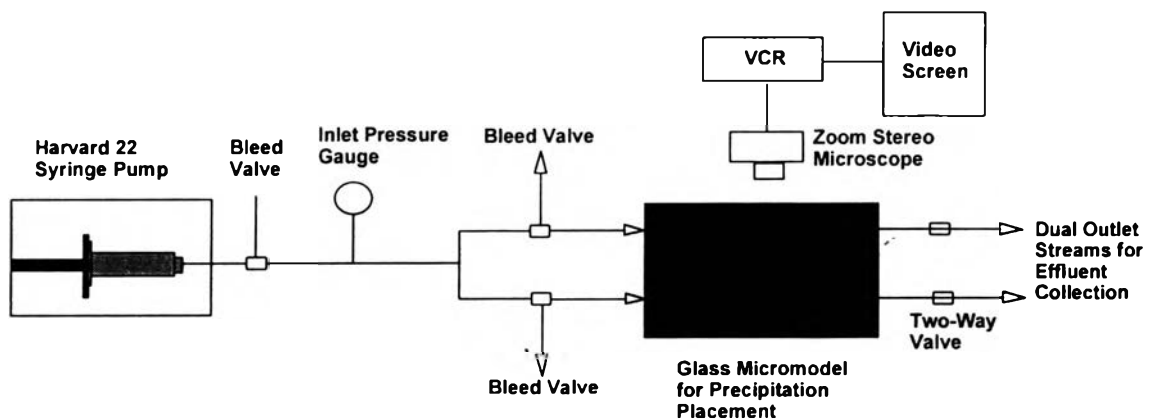


Figure 3.3 Schematic of micromodel apparatus.