

CHAPTER III

METHODOLOGY

3.1 Batch Synthesis Experiments

3.1.1 Materials

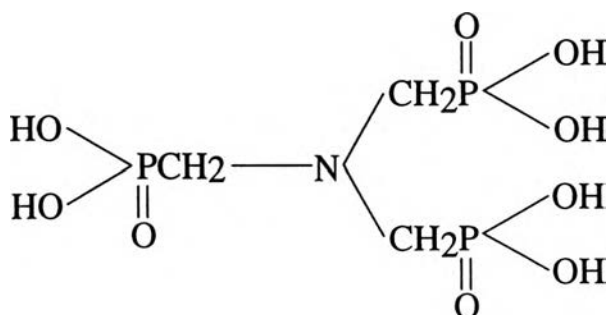
A scale inhibitor used in this study was the phosphonate Aminotri(methylenephosphonic acid) or ATMP. It contains with three active phosphate groups which offer potential reacting sites with divalent cations (see Figure 3.1). It is able to react easily with calcium and to form precipitates in different patterns. Only a few ppm of this phosphonate can dissolve scale deposition and inhibit scale formation in the system for a long period (Monsanto Technical Bulletin, No. 9023). The properties of ATMP are described in Appendix B.

ATMP solution (5% wt) used in this study was prepared by dilution of commercial ATMP solution (*MONSANTO*, 50 % wt) in deionized water.

Calcium solution (CARLO ERBA) was used as divalent cation for reacting with ATMP to form soluble salts. A 0.5 M Ca^{2+} solution was prepared by dilution of calcium chloride anhydrous in DI water.

Potassium hydroxide (AJAX CHEMICAL) and hydrochloric acid (J.T. BAKER) were used for adjusting the desired pH of the system while ensuring that the concentration of the solution did not change.

Both ATMP and calcium solution were titrated in amount of 1:1 and 10:1 molar ratios to form sparingly soluble precipitates.



Molecular Weight : 299

Color : Pale yellow in solution

Specific Gravity in Solution (20/20°C) : 1.33

pH, 1% Solution at 25°C : < 2

Acidity constants in 1.0 Molar KNO₃ at 25°C :

pK ₁	< 2	pK ₄	= 5.46
pK ₂	< 2	pK ₅	= 6.66
pK ₃	= 4.30	pK ₆	= 12.3

Figure 3.1 Properties of Aminotri(methylenephosphonic acid)
(Monsanto Technical Bulletin, No. 9023).

3.1.2 Experimental System and Procedure

A schematic of the apparatus used in this study is shown in Figure 3.2. A phosphonate solution (ATMP) was placed in a beaker and it was stirred continually by using a magnetic stirrer. A pH electrode was placed into the solution to measure pH during titration with calcium solution. Concentrated KOH and HCl solutions were used for adjusting pH of ATMP solution in the beaker to the desired pH value.

The titrations were carried out at 25 °C. The ATMP solution was titrated in 5 ml increment of calcium solution until the titration was completed. After the titration, the resulting solution was left for 24 hrs in the beaker where the precipitate formed. The resulting precipitate was filtrated by using 0.22 micron filter paper and left to dry in an oven at 100 °C until constant weight. Finally, the dried precipitates were then analyzed for their properties.

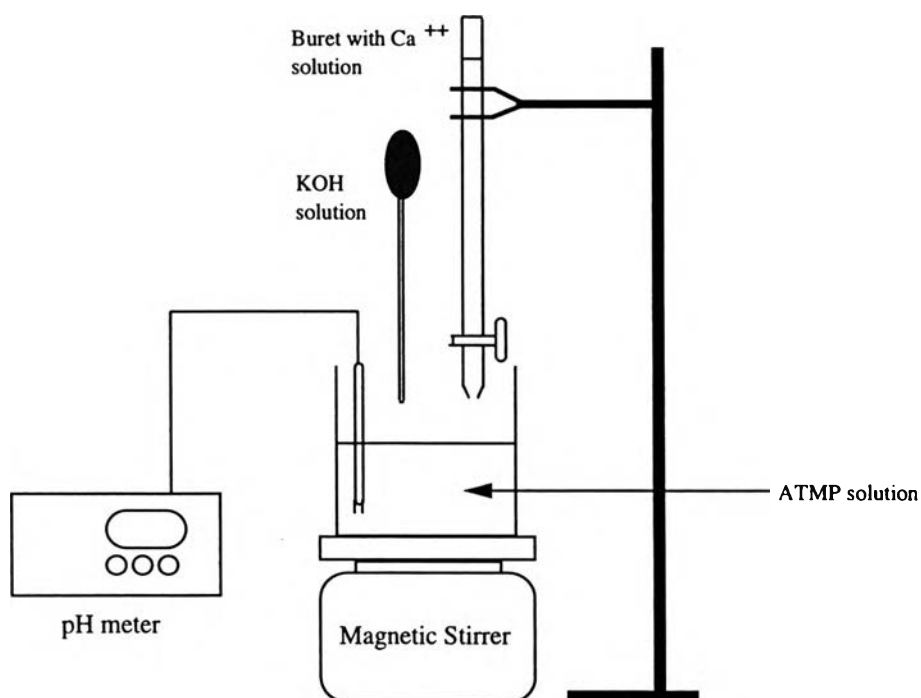


Figure 3.2 Schematic of Batch Synthesis Apparatus.

3.1.3 Characterization Techniques

The precipitate was divided by three samples for analyzing its properties. Figure 3.3 illustrates the characterization procedure of the resulting precipitates. The methodology of each technique is described below:

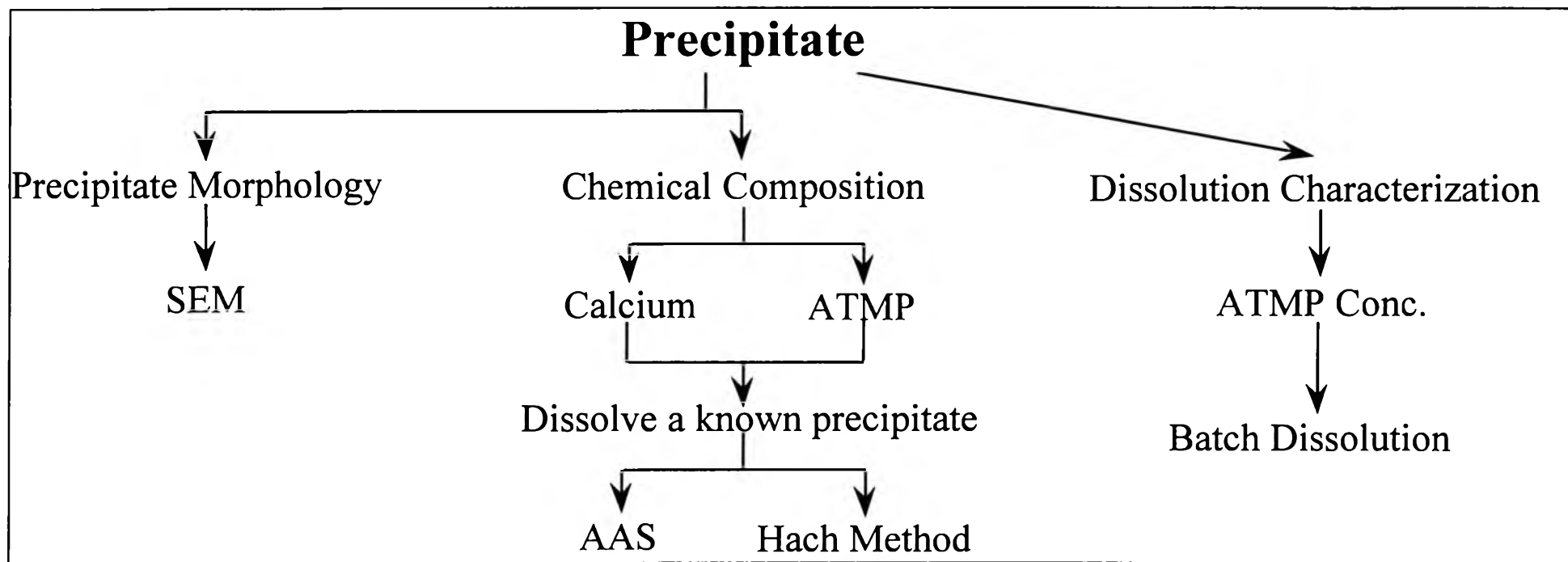


Figure 3.3 Flow Chart of the Characterization Procedures.

Precipitate Morphology. The morphology of resulting precipitate was studied by using Scanning Electron Micrograph (SEM) and X-ray Diffraction (XRD).

Chemical Composition. The calcium to ATMP molar ratio in the precipitate is necessarily known for classifying the type of precipitate formed. A known amount of precipitate was dissolved in acidic solution and prepared in a volumetric flask. Calcium concentration was analyzed by Atomic Adsorption Spectrophotometer (AAS, Perkin-Elmer 3100) while ATMP concentration was analyzed by Spectrophotometric method given by Hach technique. This technique, 25 ml of ATMP solution was oxidized in the presence of persulfate under UV light for ten minutes to orthophosphate. The orthophosphate formed was then reacted with a molybdate reagent to yield phosphate. Finally, the phosphate concentration was measured by using a UV spectrophotometer.

Precipitate Solubilities. The solubilities of precipitates obtained from various molar ratios of the precipitating calcium/ATMP were determined by using batch dissolution experiment. The excess precipitate was placed in a beaker and then DI water was gradually added for dissolving it with stirred condition for ensuring that the equilibrium would approach. After this reaction was performed for a long time until equilibrium, the solubility of each precipitate was obtained.

3.2 Precipitate Performance in Porous Media

To study the release mechanism of calcium-ATMP precipitates in porous media, both micromodel experiments and coreflood experiments were performed.

3.2.1 Experimental System of Coreflood

A schematic of the experimental apparatus used for coreflood experiments is shown in Figure 3.4. One inch diameter and three to five inch length ceramic cores (K~33 mD, porosity~40%) were placed in a Hassler Cell where an overburden pressure was applied. The ceramic cores used in this experiment were comprised of silicon dioxide and aluminum oxide.

Fluid (DI water or phosphonate solutions) was pumped through the core by using an FDS-210 pumping unit. An accumulator containing the inhibitor solution was placed in-line with the system in order to hold the desired pumping solution. DI water was pumped into the accumulator at the bottom where it replaced the holding fluid, resulted in the desired volume of inhibitor solution flowing into the core. Pressure taps were placed at various positions down the length of the core for pressure measurements: at the core inlet, 0.5 inches into the core, and 1.5 inches into the core. A 0.22 micron filter was placed in-line with the entering fluid to collect any foreign particles. The effluents were collected in 20 ml vials at interval times and then analyzed for phosphonates.

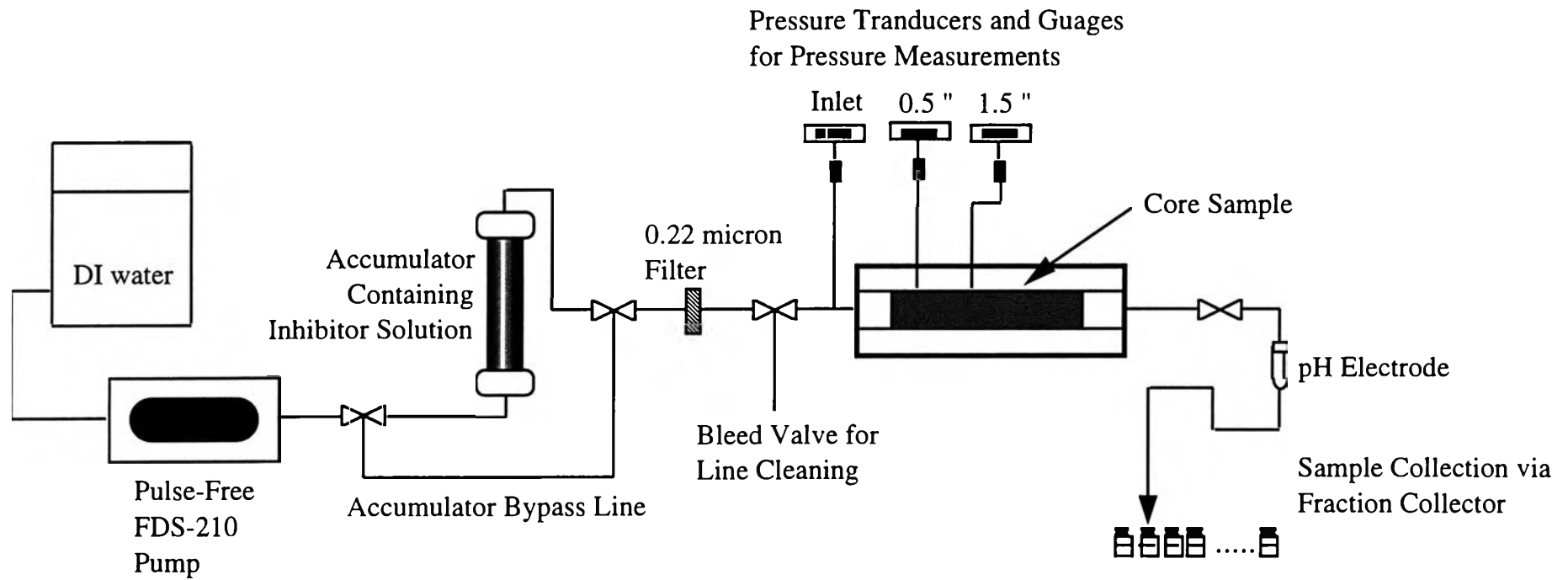


Figure 3.4 Schematic of Coreflood Experiment.

The procedure for precipitation and dissolution of calcium-ATMP in the coreflood experiment was described as follows. Firstly, the core was filled up with DI water in order to determine its initial permeability with Darcy's law. Next, a supersaturated calcium-phosphonate (ATMP) solution was pumped continually through the core until the effluent ATMP concentration matched that of the inlet concentration. To ensure that the core was completely dispersed with this supersaturated solution, 3-5 pore volumes was shut-in. The placement process should be presented in the induction period (1-2 hours).

The solution was shut-in in the core for a desired period (1-2 days) for allowing in-situ precipitation to occur. After this shut-in, the core was eluted by DI water for dissolving the precipitate in the core and then the effluent samples were collected and analyzed the concentration of ATMP.

3.2.2 Experimental System of Micromodel

The micromodel experiments were performed by using an etched glass presented as porous media. Figure 3.5 illustrates the setup of the micromodel unit. The micromodel unit offers several advantages which one can see the mechanisms of precipitation and dissolution occurring simultaneously in porous media. The micromodel (PV ~ 0.1 cc.) was used in this experiment. A Harvard 22 syringe pump was used to flow a desired fluid into the micromodel via two inlet streams. The two inlet streams was to ensure that the fluid was spread uniformly throughout the entire micromodel space. The effluent was also collected via two outlet streams. All the tubing used in this set was 1/16 inch diameter, and could stand at a high pressure.

The development in the micromodel was observed through a stereo-zoom microscope and recorded by using a super VHS video recorder.

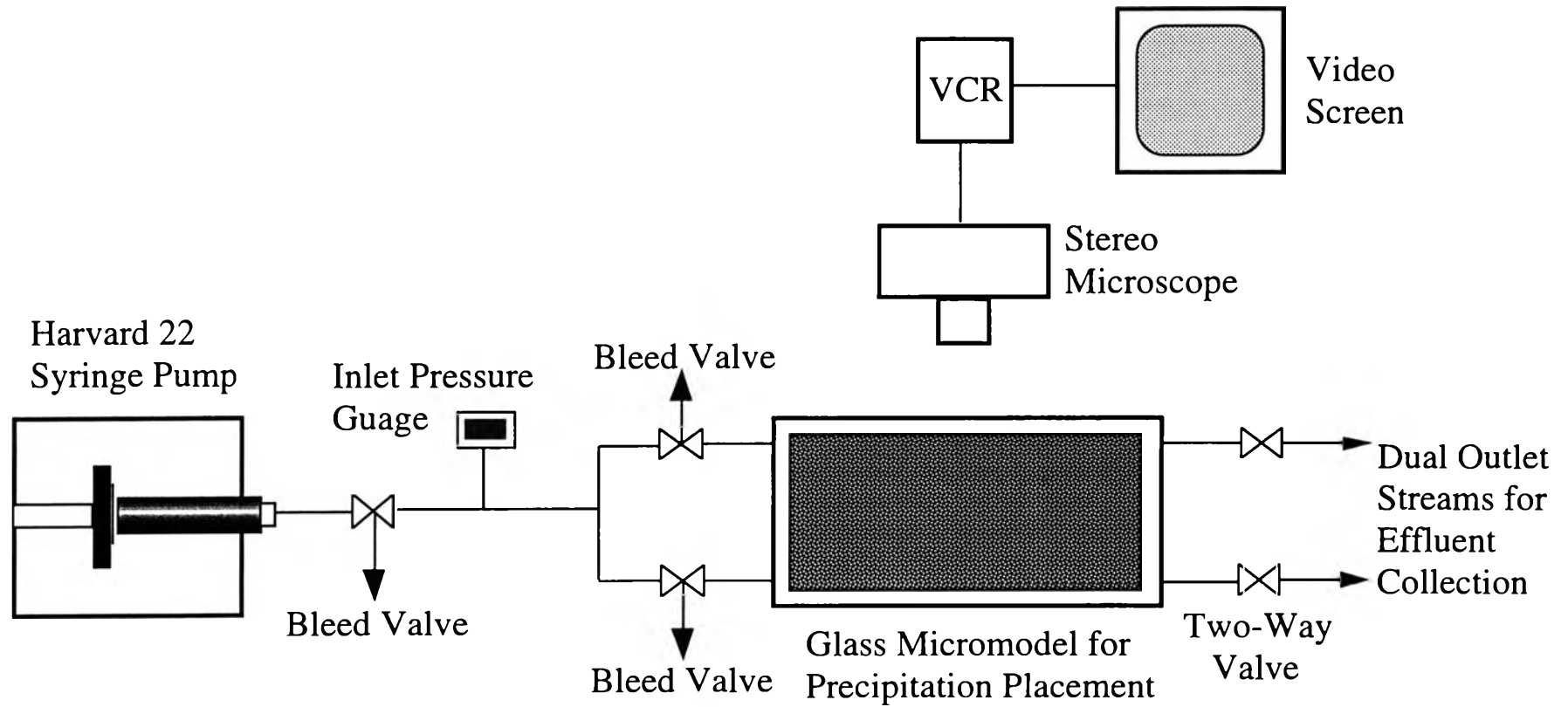


Figure 3.5 Schematic of Micromodel Experiment.