

CHAPTER III EXPERIMENTAL SECTION



3.1 Materials

A scale inhibitor used in this study was the phosphonate Aminotri(methylenephosphonic acid) or ATMP. It contains three active phosphate groups that offer three potential reactive sites with divalent cations (see Figure 3.1). It is able to react easily with calcium and to form precipitates in different patterns. Only 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 A.

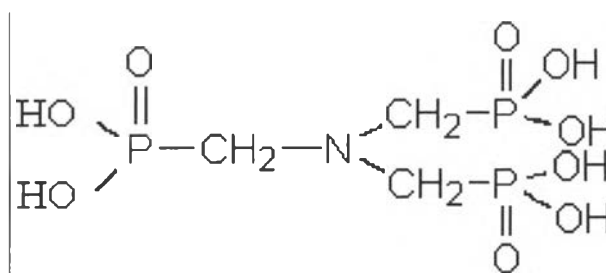


Figure 3.1 Molecular structure of ATMP.

ATMP solution (Solution, Dequest2010) used in this study was prepared by dilution of commercial ATMP solution (MONSANTO, 50%wt) with deionized water.

Calcium solution (Analytical Grade) was used as divalent cation for reacting with ATMP to form soluble salts. A 5 M Ca^{2+} solution was prepared by dilution of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) with deionized water.

Sodium, Lithium, and Potassium solutions were used to study the effect of cation on precipitation reaction. 5M Solution of Na^+ , Li^+ and K^+ were prepared by dilution of analytical grade reagents of NaCl , LiCl , and KCl with deionized water, respectively.

Potassium hydroxide and hydrochloric acid were used for adjusting any desired pH of the system while ensuring that the concentration of the solution did not change.

3.2 Experimental Set-ups and Procedures

3.2.1 Ca - ATMP Nucleation Experiments

The experimental procedures are described briefly below. A desired amount of ATMP solution and deionized water were placed in a 250 ml glass reactor and stirred continuously by a magnetic stirrer. The pre-determined volume of a 5% KOH solution was added to obtain the desired solution pH. The solution turbidity at a wavelength of 500 nm was measured by circulating the solution through the quartz flow cell placed in a UV/Vis Spectrophotometer at constant flow rate. Figure 3.2 shows the experimental set-up of nucleation study.

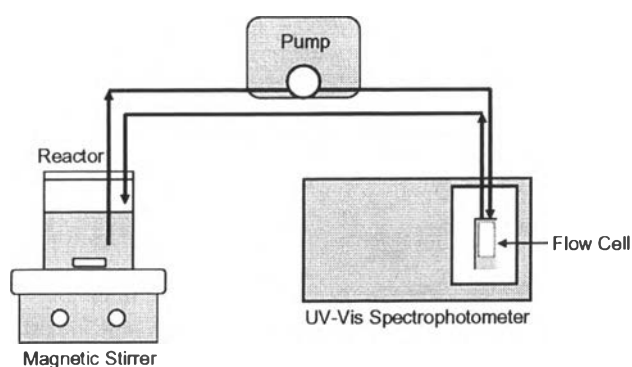


Figure 3.2 Experimental apparatus for nucleation experiments.

A required quantity of CaCl_2 solution was added into the reactor. An increasing adsorption was observed at the point where solution became turbid. The

experiment was continued until the turbidity no longer changed significantly. After each run, the precipitating solution was transferred and the apparatus was rinsed with 1 M aqueous HCl solution to remove residual precipitate. The solution was left for a week in a closed flask at ambient temperature. In the case of salt effect investigation, the precipitation procedure was the same as in absence of salt, except that NaCl, LiCl or KCl solution was mixed together with the inhibitor solution in the reactor before addition of CaCl₂ solution. All precipitation experiments were carried out at room temperature (25°C) and an equimolar concentration of calcium chloride and ATMP was maintained constant. The equilibrium concentration of ATMP in the supernatant was determined using the Hach technique, in which a sample of solution was oxidized to orthophosphates by adding a standard amount of persulfate. The resulting solution was next exposed to ultraviolet light causing phosphate groups to break off. The phosphate concentration was then determined using a UV-Vis Spectrophotometer with the aid of a coloring reagent.

3.2.2 Ca-ATMP Growth Experiments

The growth rates of Ca-ATMP precipitates were determined at different supersaturation levels of the Ca-ATMP solution. The supersaturated solutions of Ca-ATMP were prepared by mixing the solutions of CaCl₂ and ATMP. The solution pH was adjusted to any desired value by adding small amount of concentrated KOH solution as needed. A seed solution of 10%wt Ca-ATMP particles in its saturated solution was prepared. The growth reaction of Ca-ATMP on seed was initiated by adding the seed solution into the supersaturated solution. The resultant solution was then left on a shaker apparatus to allow the precipitate to grow under constant mixing condition. After 20 min, a small amount of solution was sampled and the Ca-ATMP particles were separated and dried at 70°C. Weights of Ca-ATMP particles before and after were used to calculate a growth rate of the system. The initial molar ratios of CaCl₂ to ATMP were kept constant at 1:1 ratio. The initial concentration of CaCl₂ and ATMP were varied from 0.042 M to 0.09 M. When any monovalent salt (Na⁺, Li⁺, or K⁺) was added into the solution to investigate the effect of monovalent salt on the Ca-ATMP growth rate, the procedure was the same

as in the absence of salt, except the salt solution was added in the reactor before adding seed.

3.2.3 Characterization of Ca-ATMP Precipitates

In order to study the morphology and size of Ca-AMP precipitates, a small amount of resulting precipitate-containing solution was collected and then filtered out using a 0.22-micron filter membrane. The membrane filters holding Ca-ATMP precipitates were then washed with deionized water, dried at 70°C for a day and then placed on the holders to be ready for the characterizations. The morphologies of Ca-ATMP precipitates formed at different conditions were examined by using a Scanning Electron Microscope (SEM) (Philips, XL 30FEG). A qualitative analysis of elemental compositions of the precipitates was simultaneously investigated by using an Electron Dispersive X-ray Analyzer (EDX).