

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

The commercial phosphonate scale inhibitor used in this study was Amino trimethylene phosphonic acid or ATMP having three active phosphate groups available for reacting with divalent cations. The chemical structure and physical properties of this phosphonate scale inhibitor are described in Figure 3.1. This phosphonate scale inhibitor was selected as the model because it contains multiple active phosphate groups and commonly used in the petroleum field. ATMP solution was directly prepared by dilution of commercial ATMP solution (50% active content) with deionized water.

Calcium solution (analytical grade) was used as the model divalent cations for reacting with ATMP to form the soluble precipitates. A calcium concentration of 5.0 M was prepared by dissolving a desired amount of calcium chloride anhydrous ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water. This concentration almost reached its solubility, which can save time during titration.

Magnesium solution (analytical grade) was also used to study the effect of magnesium ion on Ca-ATMP precipitates. A magnesium concentration of 3.0 M was prepared by dissolving a desired amount of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) as well.

Potassium hydroxide and hydrochloric acid (analytical grade) were used for controlling the precipitating solution pH during titration. The maximum concentration of these materials was prepared to ensure that the concentration of the solution did not change significantly.

Sodium chloride solution (analytical grade) was also involved in this study for investigating the effect of ionic strength on the precipitate formation.

A desired amount of sodium chloride powder was dissolved in deionized water for preparing the concentration of 5.0 M.

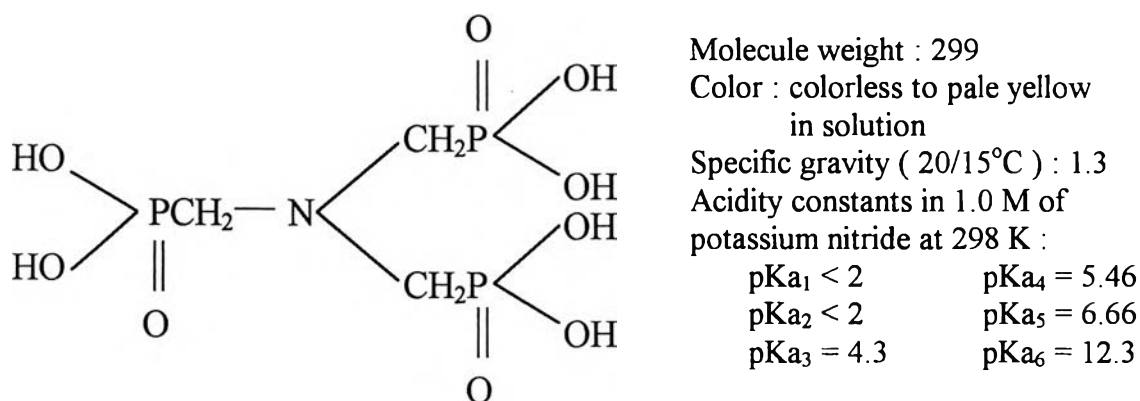


Figure 3.1 Molecular structure and its properties of ATMP phosphonate.

3.2 Batch Synthesis Experiments

The experiments in this section were conducted to synthesize the divalent cation-scale inhibitor precipitates under different conditions using a simple titration. In this study, there were three main parts as described below.

3.2.1 Ca-ATMP Precipitation Batch Synthesis

A schematic of simple titration apparatus used in this study was illustrated in Figure 3.2. A desired amount of phosphonate solution (ATMP) was placed in a spherical flask and stirred continuously by using a magnetic stirrer. Nitrogen gas was flowed continuously into the solution to minimize the effect of atmospheric carbon dioxide resulting in reduction of the solution pH. A pH electrode was placed into the precipitating solution to monitor the solution pH throughout the titration. All titrations were carried out at room temperature (at 25 °C). A small amount of crushed potassium hydroxide was put in the ATMP solution until the desired solution pH was obtained. Next,

calcium solution placed in a buret was being slowly introduced into the ATMP solution until the titration was completed.

For conducting titration, potassium hydroxide and concentrated hydrochloric acid were used to maintain the precipitating solution pH. After this titration was achieved, the resulting slurry solution was left for a week to ensure that it reached precipitation equilibrium. The resulting precipitates were then filtered out using 0.22 micron filter membrane papers and washed with deionized water to eliminate the remaining solution. Finally, the resulting precipitates were dried in the oven at 85°C for 24 hours. The precipitate samples were kept in a dessicator for the dissolution experiment as well as they would be characterized which will be described in the next section.

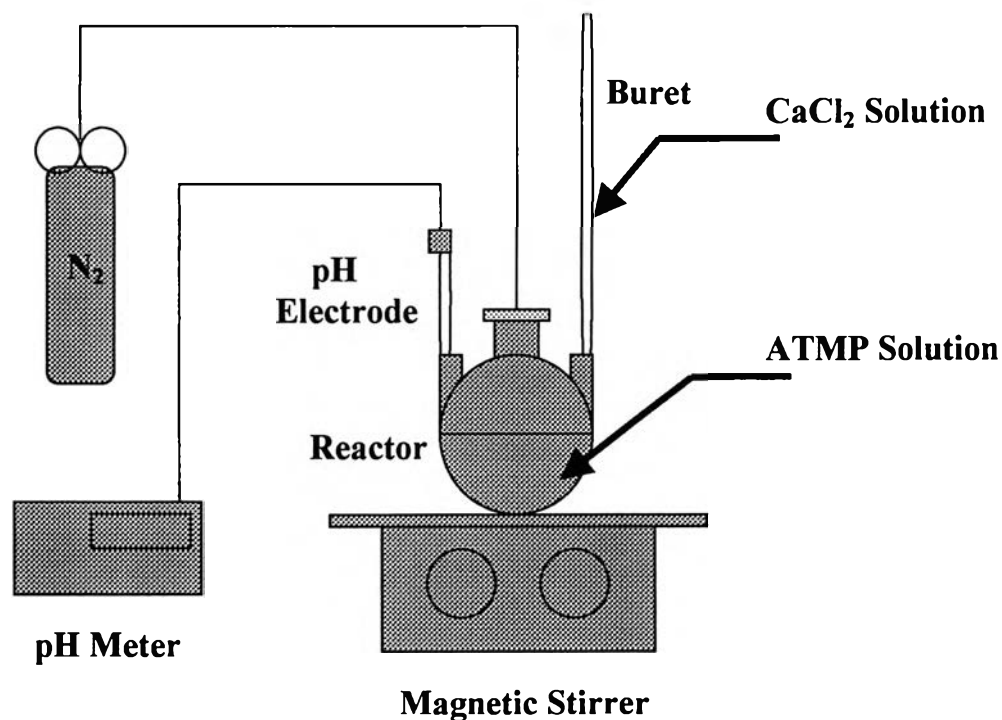


Figure 3.2 Schematic of batch synthesis apparatus for Ca-ATMP precipitation.

3.2.2 Mg-ATMP Precipitation Batch Synthesis

For the synthesis of Mg-ATMP precipitates, all apparatus and procedures were exactly the same as Ca-ATMP precipitation batch synthesis except that magnesium solution was placed in a buret instead of calcium solution.

3.2.3 Ca-ATMP Precipitation Batch Synthesis in the Presence of Magnesium Ion

Magnesium and phosphonate scale inhibitor solution (ATMP) were mixed together in a spherical flask and stirred continuously. This mixed solution was then added with small amount of crushed potassium hydroxide and concentrated hydrochloric acid for adjusting the solution pH. After the desired solution pH was obtained, the solution was being gradually titrated with calcium solution placed in a buret. All apparatus and other procedures were the same as Ca-ATMP precipitation batch synthesis. The concentration of magnesium in the system was systematically varied in terms of the total Ca/Mg molar ratios whereas the total calcium concentration was kept constant. Precipitating solution pHs, Ca/Mg molar ratios in the precipitating solution and molar product ($[Ca][ATMP]$) were similar to Ca-ATMP precipitation batch synthesis.

3.3 Batch Dissolution Experiments

The initial dissolution rate of the resulting precipitates was investigated by using a rotating disk reactor as shown in Figure 3.3. As a surface area of precipitates affects the initial rate of dissolution, it becomes essential to control this factor in every batch dissolution experiment. To keep the surface area constant, a 0.10 g of the crushed precipitate was used to make a pellet by using hydraulic press with a highly polish stainless steel punch and

die having a diameter of 13 mm. The sample was compressed at 500 psi with 0.5 minutes dwelling time to obtain smooth. A diameter and thickness of this pellet were 1.30 cm and 0.10 cm, respectively. A pellet was attached to the center of a rotating disk connected with the rotating disk holder. Then, the rotating disk was rotated using a velocity of 1,000 rpm, the resulting precipitate in a pellet form was slowly dissolved back in a 200 ml of deionized water. The concentration of divalent cations was measured with respect to time and the initial rate of dissolution was directly determined from a slope of graph plotted between the concentration of divalent cations and time.

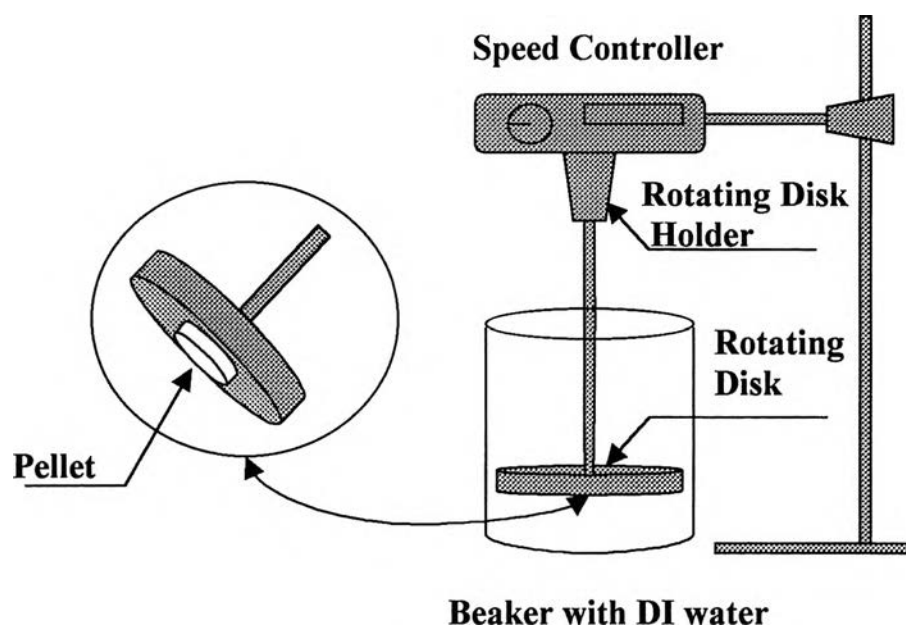


Figure 3.3 Schematic of rotating disk reactor for batch dissolution.

3.4 Characterization Techniques

3.4.1 Chemical Compositions Analysis

To classify types of the resulting precipitates, the divalent cations to phosphonate molar ratios in precipitates had to be examined. These molar ratios were determined by dissolving a known amount of the resulting precipitates in an acidic solution. Divalent cation concentration (Ca or Mg in this work) were analyzed by using an Atomic Absorption Spectrophotometer (AAS, Perkin-Elmer 3100), while phosphonate concentration (ATMP) was measured by Hach technique. In this technique, a 25 ml of phosphonate solution was oxidized in the presence of persulfate under UV light for ten minutes to yield orthophosphate. This orthophosphate solution was then reacted with a molybdate reagent to form phosphate. This formed phosphate solution was finally analyzed by using a UV spectrophotometer.

3.4.2 Morphology and Structure Analyses

The morphologies of the resulting precipitates were directly examined by using Scanning Electron Microscope (SEM), while the crystalline or amorphous structures of the precipitates were studied by using X-ray Diffraction (XRD).