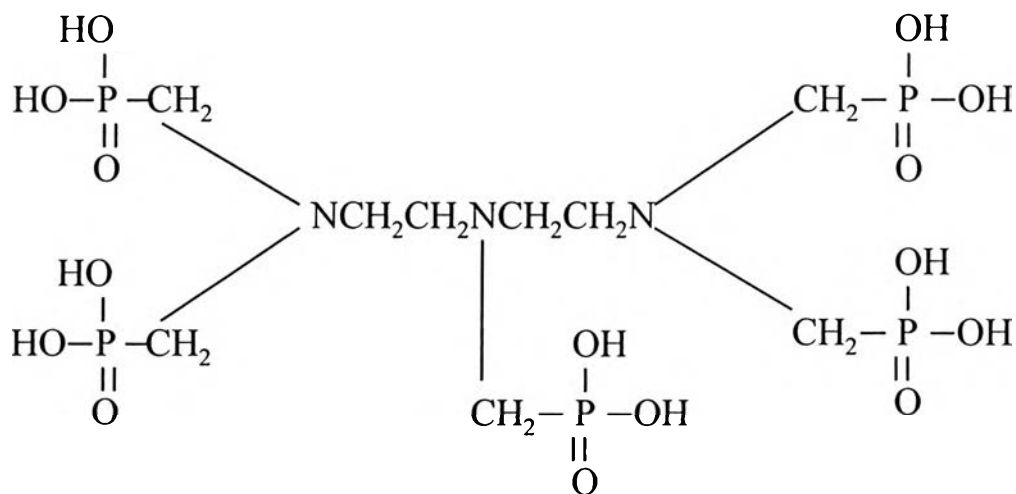


CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

The phosphonate used in this study was diethylenetriaminepenta (methylenephosphonic acid, DTPMPA) containing five active phosphate groups, offering potential reacting sites with divalent cations. Figure 3.1 illustrates molecular structure and chemical properties of DTPMPA.



Diethylenetriaminepenta (methylenephosphonic acid) (DTPMPA)

Typical Analysis

Active content: 50% as phosphonic acid
Molecular Weight: 573
Color: amber solution
Specific gravity (20°/50°): 1.4
pH of 1% solids solution: < 2

Acidity constant in 0.1 M KCl at 298 K

pK1 < 1 pK6 = 6.38
pK2 < 1 pK7 = 7.17
pK3 = 2.80 pK8 = 8.15
pK4 = 4.45 pK9 = 10.10
pK5 = 5.50 pK10 = 12.04

Figure 3.1 Molecular structure and properties of DTPMPA.

Calcium chloride dehydrated (CaCl_2 97%) was used to react with phosphonate for synthesis of calcium-DTPMPA precipitates. During titration process, crushed potassium hydroxide (KOH 85%) was used to stabilize pH of solution.

3.2 Batch synthesis

The DTPMPA solutions used in this study were prepared by mixing the desired amount of DTPMPA in deionized water. Calcium is the divalent cation in the precipitate, which commonly forms scale in many oil fields. Hence, calcium chloride was used as divalent ion in this study. The calcium solutions were prepared by dissolving the desired amount of calcium chloride dehydrated in deionized water.

A schematic of the titration apparatus used for synthesis of calcium-DTPMPA precipitates is shown in Figure 3.2. Calcium was mixed with DTPMPA in 5 ml increment until the titration was completed. As pH decreased during titration, crushed potassium hydroxide was added to maintain the solution pH. After the titration was completed, the resulting solution was left to sit for a week to allow for complete precipitation. The resulting precipitate was then filtered using a 0.22 micron filter and washed with deionized water to remove all dissolved calcium and phosphonate. The precipitate was finally dried at 80 °C for 48 hours.

3.3 Characterization techniques

The synthesized precipitates were characterized in three different ways. The methodology of each technique is described below.

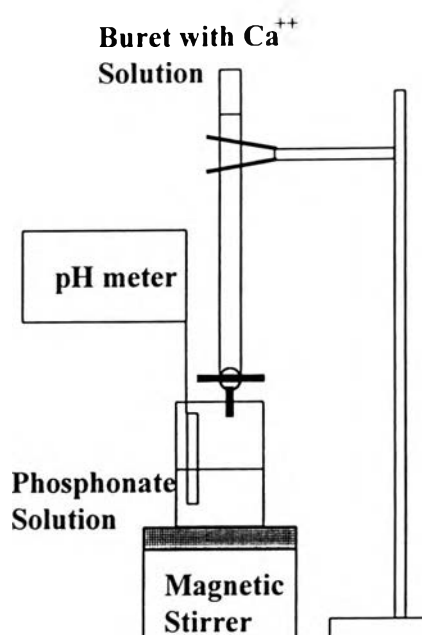


Figure 3.2 Schematic of titration apparatus used to synthesize calcium-DTPMPA precipitates.

3.3.1 Chemical composition

The chemical compositions of all the precipitates, i.e. the calcium to DTPMPA molar ratio of the precipitate, were done by dissolving a known amount of calcium-DTPMPA precipitate in an acidic solution. The dissolved precipitate was then diluted by deionized water to the fixed volume. The solution concentrations of both calcium and DTPMPA were then analyzed. Calcium content was determined by using an atomic adsorption spectrophotometer (AAS, Perkin-Elmer 3100). DTPMPA concentration was measured by the Hach technique. Phosphonate was oxidized to orthophosphate in the presence of persulfate and ultraviolet light. Orthophosphate was then reacted with a molybdate reagent to form phosphate. The resulting phosphate was finally analyzed by a spectrophotometer.

3.3.2 Dissolution study

A known amount of the ground precipitate was dissolved in deionized water, while pH and DTPMPA concentration were analyzed as a function of time during the dissolution process. The solubility equilibrium of each precipitate was measured by adding excess amount of the precipitate in deionized water.

3.3.3 Precipitate morphology

A scanning electron microscope (SEM) was used to determine morphologies of all the synthesized precipitates.

3.4 **Micromodel experiment**

A schematic of the experimental apparatus used in this study is shown in Figure 3.3. The simulated porous media consisted of two-dimension glass etched micromodels (pore throat diameters ranged from 50-300 microns with a total pore volume of approximately 0.2 ml.). Having pore throats for porous medium simulation, the precipitate was placed and the release process was observed by stereo zoom microscope and VCR. A syringe pump was used to introduce deionized water into the micromodel while the pressure drop throughout the micromodel was measured by a pressure transducer.

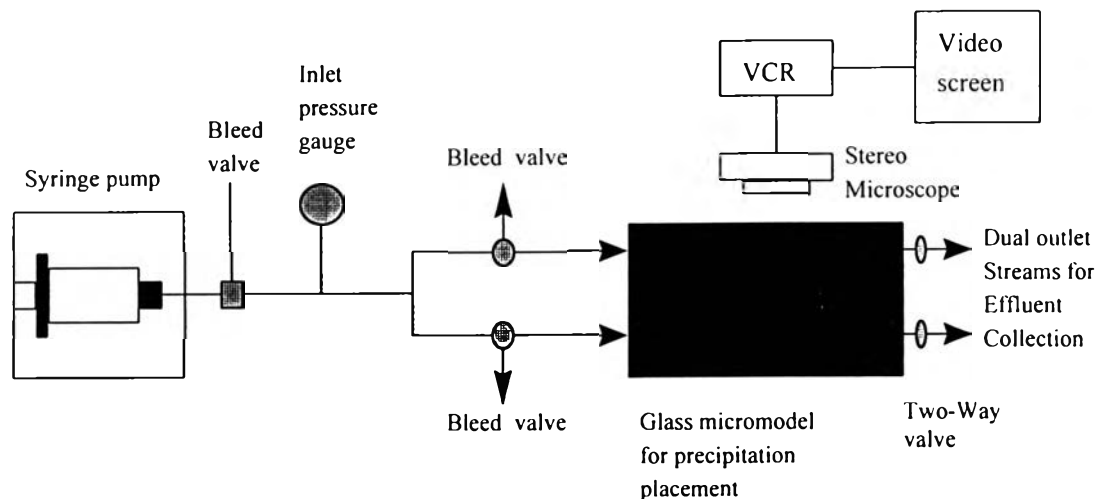


Figure 3.3 Schematic of micromodel apparatus used to test performance for calcium-DTPMPA precipitate in porous media.

This micromodel experiment was designed to simulate an actual condition in oil fields. A supersaturated calcium-DTPMPA solution was placed into the micromodel to achieve the saturation. The induction period was 1-2 hours following which the supersaturated solution sat in the micromodel approximately 24 hours. After a shut-in period, the precipitate in the micromodel was dissolved by deionized water and the effluent was collected. The Hach technique was used to analyze the effluent DTPMPA concentration. During the elution process, the release mechanism of the calcium-DTPMPA precipitates was visually observed and recorded by using VCR with stereo zoom microscope. These images and the elution curve could reveal a clear understanding of the exact release mechanism.