

CHAPTER III

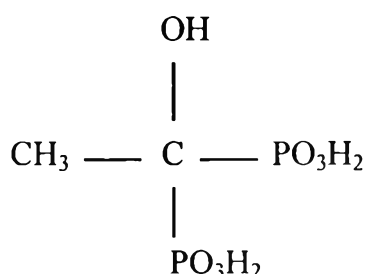
EXPERIMENTAL SECTION

3.1 Chemicals

The phosphonate scale inhibitor used in this study was 1-Hydroxyethylidene-1, 1-diphosphonic acid (HEDP) containing two active phosphate groups, which offer two potential reacting sites, with divalent cations. This phosphonate was used for three main reasons:

- 1) It has been shown to inhibit a wide variety of scales in substoichiometric amounts.
- 2) Its concentration can be easily and accurately analyzed by oxidation and colorization techniques.
- 3) It is the easiest structure and commonly used in the petroleum field.

Figure 3.1 illustrates molecular structure and Table 3.1 shows the chemical properties of HEDP.



1-Hydroxyethylidene-1, 1-diphosphonic acid, HEDP

Figure 3.1 Molecular structure of HEDP (Monsanto technical bulletin, Dequest 2010)

Table 3.1 Chemical properties of HEDP (Acid constants of HEDP in 0.5 M tetramethylammonium chloride at 25°C)

Molecular weight	206
Description	Clear solution, free form solids
Color, APHA (Hazen)	150 Maximum
Total Active Acid Content, %	58.0 – 62.0
Phosphorous Acid, %	4.0 Maximum
Acetic Acid, %	1.0 Maximum
pH of 1% solution at 25 °C	2.0 Maximum
Iron (as Fe), ppm	20 Maximum
Chloride (as Cl), ppm	100 Maximum
Specific Gravity (20/20 °C)	1.430 – 1.471
$\text{HEDP} \rightleftharpoons \text{HEDP}^- + \text{H}^+$	$\text{pK}_1 < 1$
$\text{HEDP}^{-2} \rightleftharpoons \text{HEDP}^{-2} + \text{H}^+$	$\text{pK}_2 = 2.54 \pm 0.05$
$\text{HEDP}^{-2} \rightleftharpoons \text{HEDP}^{-3} + \text{H}^+$	$\text{pK}_3 = 6.97 \pm 0.05$
$\text{HEDP}^{-3} \rightleftharpoons \text{HEDP}^{-4} + \text{H}^+$	$\text{pK}_4 = 11.41 \pm 0.05$

The divalent cation used in this study was calcium. This cation was present in solution in the form of calcium chloride. Calcium was used to react with HEDP to form Ca^{2+} /HEDP precipitates.

In this thesis, there were three main parts to be carried out:

- 1.) Batch Experiment
- 2.) Differential Reactor Experiment
- 3.) Glass Micromodel Experiment

3.2 Batch Experiment

3.2.1 Ca^{2+} /HEDP Precipitation Synthesis and Characterization

The apparatus used to synthesize Ca^{2+} /HEDP precipitates is shown in Figure 3.2. The HEDP solution used in this study was prepared to have the HEDP concentration of 60 % by dissolving HEDP in deionized water. The calcium solutions were prepared by dissolving desired amounts of calcium chloride dihydrate in deionized water. All titrations were carried out at room temperature ($\approx 25\text{ }^\circ\text{C}$) and at two different pHs (2 and 6)

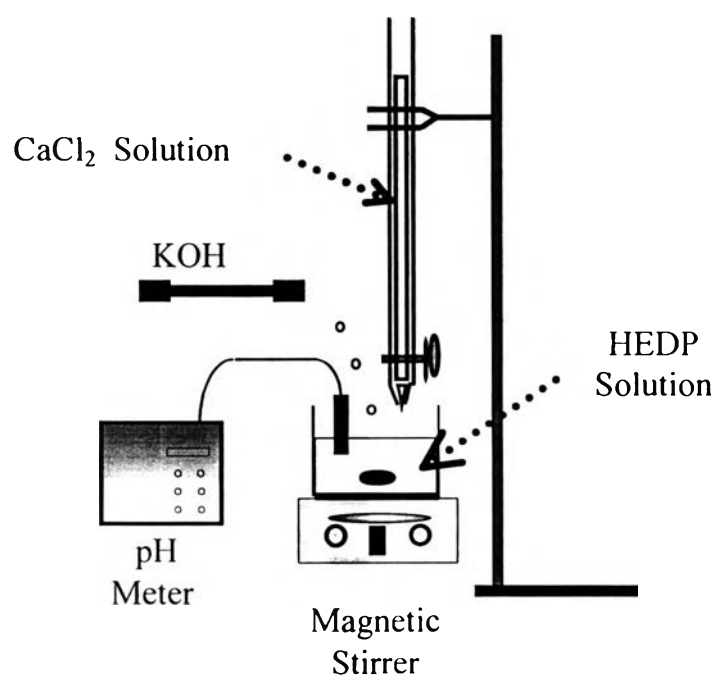


Figure 3.2 Experimental setup for Ca^{2+} /HEDP precipitate synthesis

Calcium chloride solution was added into the HEDP solution in 5 ml increments until the titration was completed. During titration, the solution was continuously stirred with a Teflon-coated magnetic stirring bar. A pH electrode was carefully placed in the reaction batch to monitor the pH of the solution throughout the experiment. pH during titration was kept constant by adding crushed KOH or concentrated HCl solution to the solution. The resulting solution was mixed for approximately 24 hours to ensure complete precipitation.

The resulting slurry was filtered using a 0.22 micron polymeric filter membrane (Millipore) and washed with deionized water to remove interstitial precipitating solution. The precipitate was then left to dry at 70 °C for 24 hours. The precipitate now was ready for analysis.

The precipitates were next analyzed to determine the molar ratio of calcium to HEDP. To do this, the known amount of precipitate was re-dissolved in deionized water where concentrations of calcium and phosphonate were determined. To determine the calcium concentration in the solution, an Atomic Absorption Spectroscopy (AAS, Perkin-Elmer 3100) was used. The phosphonate concentration was determined using Hach Technique. The Hach Technique was carried out in the following manner. First, 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 solution is colorized with a coloring agent. The phosphate concentration can then be determined using a UV-Vis Spectrophotometer.

The precipitate was also be analyzed to determine its morphology. The morphology image was visually seen through a Scanning Electron Microscope (SEM).

3.2.2 Transformation of Precipitate in Batch Experiments

A known amount of resulting 1:1 Ca²⁺/HEDP precipitate molar ratio was then placed into the Ca²⁺/HEDP supersaturated solution. The solution was continuously stirred with Teflon-coated magnetic stirring bar. This experiment was controlled at constant pH 6 by adding crushed KOH and concentrated HCl to maintain the pH of the solution. A sample of the solution was immediately collected (t=0) after placing the precipitate into the supersaturated solution and the precipitate was characterized using the same procedure as described above, in order to study the transformation as a function of time. Several samples were collected throughout approximately 24 hours for the transformation. Next, a known amount of resulting 2:1 Ca²⁺/HEDP precipitate molar ratio was placed into the pH 2 Ca²⁺/HEDP supersaturated solution, the transformation of a 1:1 Ca²⁺/HEDP was studied at a constant solution pH of 2.0.

3.3 Dissolution of Precipitates in a Differential Reactor

The dissolution rate of the precipitates was determined by using a differential reactor. A small amount of precipitate was placed between two 0.22 micron filter membranes, then held in a filter fitting as shown in Figure 3.3. A model formation water was flowed through the precipitate and the effluent was collected periodically until complete dissolution of the precipitate. The effluent samples were then analyzed for phosphonate concentration and this data was used to determine the dissolution rate of the precipitates.

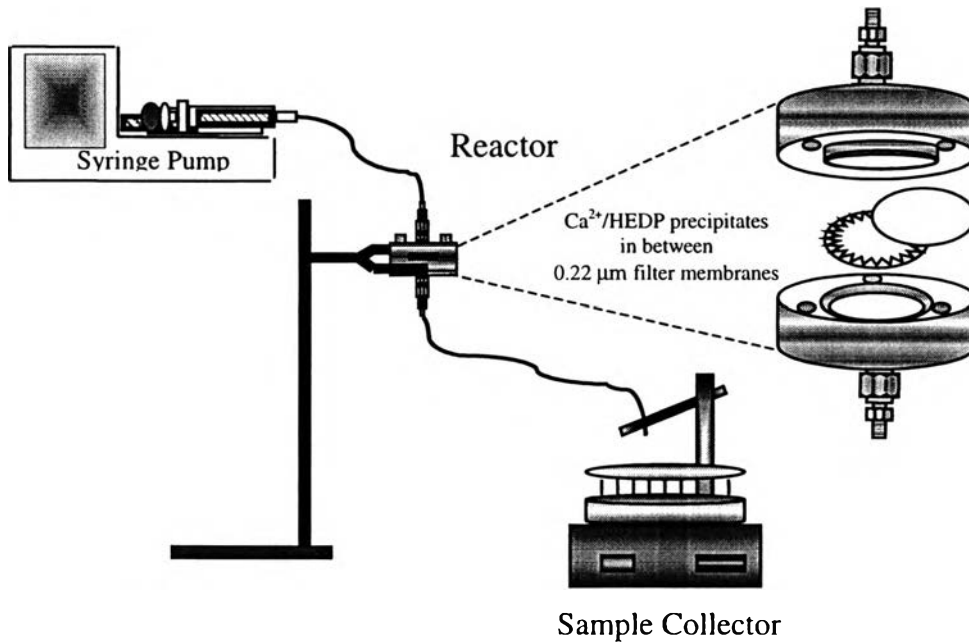


Figure 3.3 Experimental setup of differential reactor apparatus for dissolution of $\text{Ca}^{2+}/\text{HEDP}$ precipitates

Based on the data obtained from the experiment, the initial rate of $\text{Ca}^{2+}/\text{HEDP}$ precipitates dissolution, r_d , was analyzed. The integral method was chosen to express the kinetics of dissolution. The reaction rate is assumed to be first order reaction with respect to the amount of undissolved $\text{Ca}^{2+}/\text{HEDP}$ precipitate mass in batch system. If the assumed order is correct, the plot between concentration and time should be linear.

$$-r_d = \frac{dM}{dt} = -kM \quad (3.1)$$

Integrating equation (1) to obtain

$$\ln \frac{M}{M_0} = -kt \quad (3.2)$$

where k is the rate constant for $\text{Ca}^{2+}/\text{HEDP}$ precipitate dissolution (min^{-1}). M_0 and M are the amount of precipitate initially placed and the remaining of undissolved precipitate at time t , respectively.

3.4 Micromodel Experiment

The next sets of experiment were carried out in a two-dimensional glass micromodel unit having pore throat diameter ranging from 50-300 microns with a total pore volume of approximately 0.2 ml. The advantage in using the micromodel apparatus is to visualize the placement of precipitate and the inhibitor release process. The apparatus used in this experiment is shown in Figure 3.4. First, the supersaturated $\text{Ca}^{2+}/\text{HEDP}$ solution was introduced to place in the micromodel by using a Harvard 22 syringe pump. The solution was then left to sit in the micromodel for precipitation occurred approximately 24 hours under room temperature of 25 °C. The micromodel was covered with glass so it was possible to actually visualize the precipitate formation.

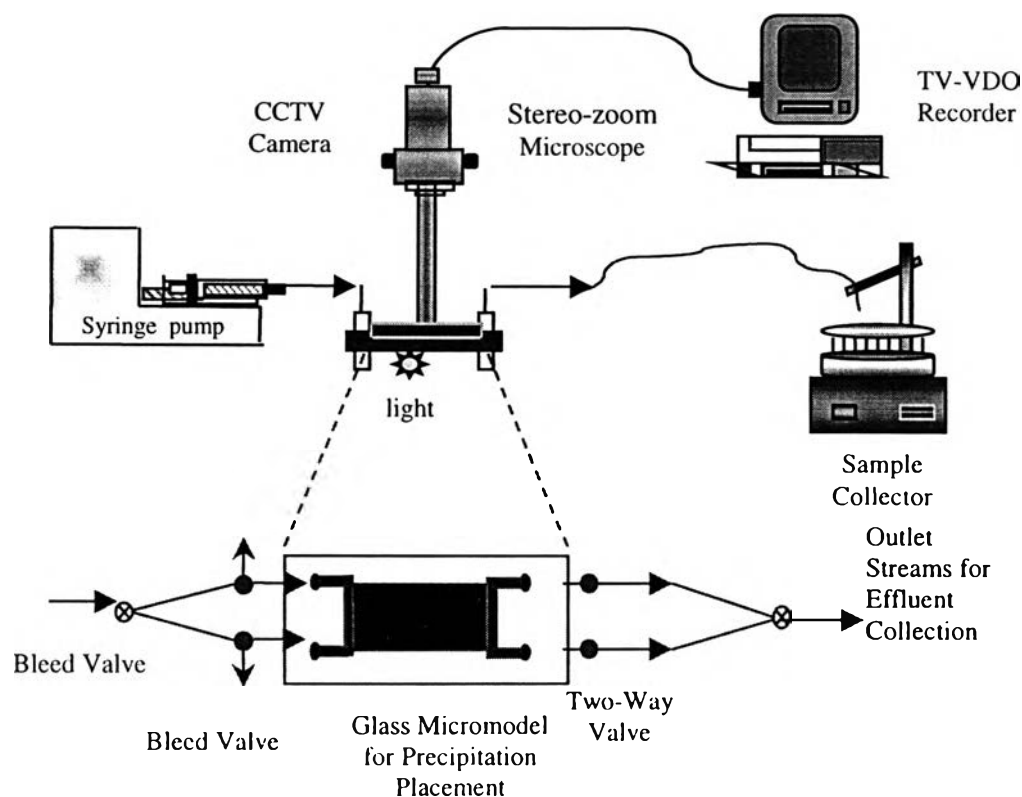


Figure 3.4 Experimental setup of micromodel apparatus used to test $\text{Ca}^{2+}/\text{HEDP}$ precipitate performance in porous media

A stereo zoom microscope with a video camera was used to transfer the micromodel image onto a monitor. Hence, by focusing on a particular area, the formation growth and subsequent dissolution of the precipitate were observed. To determine the dissolution of the precipitate in the micromodel after the shut-in period, the micromodel was eluted with deionized water or model formation water. The resulting effluents were collected and analyzed for phosphonate by using the Hach Technique.

One of important aspects of these experiments was to study exactly where the precipitates were forming in the micromodel. Another important point was to determine if the precipitates that were formed in the batch experiments could be formed in the micromodels.