



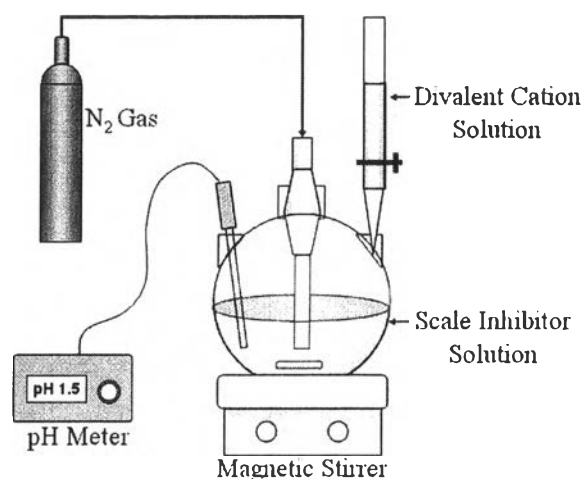
**Table 3.1** Physical properties of ATMP, DTPMP and PPCA (Browning, 1996; Solutia, 1998).

Name	Type	MW	No. of ionizable protons	Color in solution	Specific gravity	Activity constant
ATMP	Phosphanate	299	6	Colorless to pale yellow	1.3	$pK_{a1} < 2$ , $pK_{a2} < 2$ , $pK_{a3} = 4.3$ , $pK_{a4} = 5.46$ , $pK_{a5} = 6.66$ , $pK_{a6} = 12.3$
DTPMP	Phosphanate	573	10	Amber	1.4	$pK_{a1} < 1$ , $pK_{a2} < 1$ , $pK_{a3} = 2.8$ , $pK_{a4} = 4.45$ , $pK_{a5} = 5.5$ , $pK_{a6} = 6.38$ , $pK_{a7} = 7.17$ , $pK_{a8} = 8.15$ , $pK_{a9} = 10.1$ , $pK_{a10} = 12.04$
PPCA	Polymeric	1900	25	Colorless	1.2	N/A

## 3.2 Experimental Methods

### 3.2.1 Precipitation of Scale Inhibitor

A calculated amount of inhibitor solution was placed in a spherical flask, and stirred continuously by a magnetic stirrer as shown in Figure 3.2. A pH electrode was placed into the solution to monitor pH throughout the precipitation experiment. A small amount of crushed potassium hydroxide was added in the solution to obtain a desired pH. Deionized water is used to prepare all solutions. To investigate the effect of divalent cations on inhibitor precipitation, a calculated volume of divalent cations solution was added. Concentrated KOH and HCl were added dropwisely to maintain a desired solution pH. Then, the solution was left for three days in a closed flask at ambient temperature to allow precipitation. The resulting precipitates were filtered by using 0.22 micron filter membranes. The filtered precipitates were washed with deionized water and dried at 70°C. The resultant precipitates were washed again until a residue chloride was not found. Electron Dispersive X-ray Analyzer (EDX or EDAX) was used to detect chloride in the precipitate. The removal of all chloride is necessary because it interferes with the determination of precipitate composition. Ionic strength effect on precipitation of inhibitor was determined by adding NaCl into solution.



**Figure 3.2** Scale inhibitor precipitation apparatus.

### 3.2.2 Chemical Composition Analysis of Scale Inhibitor Precipitates

The divalent cations to ATMP molar ratios in the precipitates were determined by using Atomic Absorption Spectroscopy (Perkin-Elmer, 3100), and the Hach technique using a UV/Vis spectrophotometer (Varian, 300 Bio). With Hach technique, phosphonate is oxidized to orthophosphate in the presence of persulfate and ultraviolet light. The resulting phosphate concentration is analyzed using a spectrophotometer (Browning, 1996). The results were confirmed using an electron dispersive X-ray analyzer (EDX).

### 3.2.3 Precipitate Morphology Analysis

The precipitate morphologies were studied using a scanning electron microscope (Philips, XL30FEG SEM).

EDX Detector



Philips XL30FEG SEM

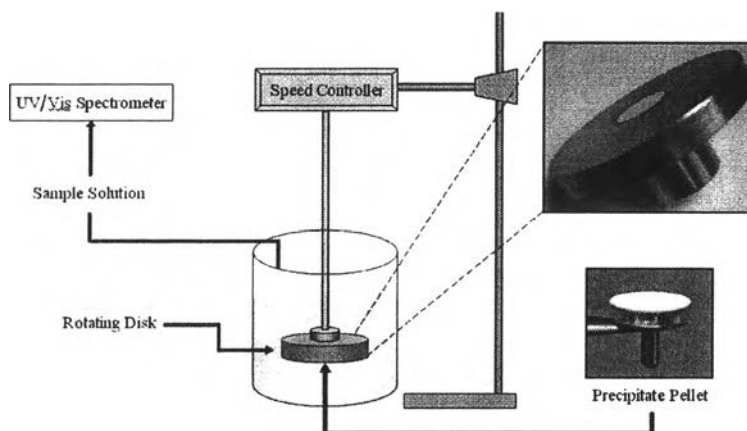
**Figure 3.3** Scanning Electron Microscope (SEM) with integrated EDAX Phoenix XEDS system.

### 3.2.4 Precipitate Crystallinity Analysis

The precipitate crystallinities were studied using a X-ray Diffractometer (XRD Rigaku, 300) with 12 kw high intensity rotary anode generator and wide-angle horizontal diffractometer equipped with low-temperature camera.

### 3.2.5 Scale Inhibitor Precipitate Dissolution Experiments

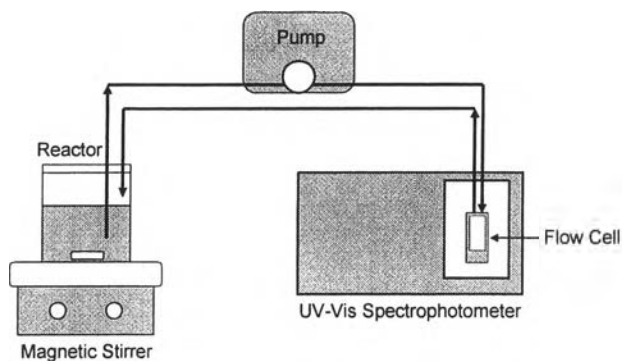
The initial dissolution rate of the inhibitor precipitate was measured using a rotating disk reactor as shown in Figure 3.4



**Figure 3.4** Schematic of the rotating disk apparatus.

### 3.2.6 Induction Time Determination

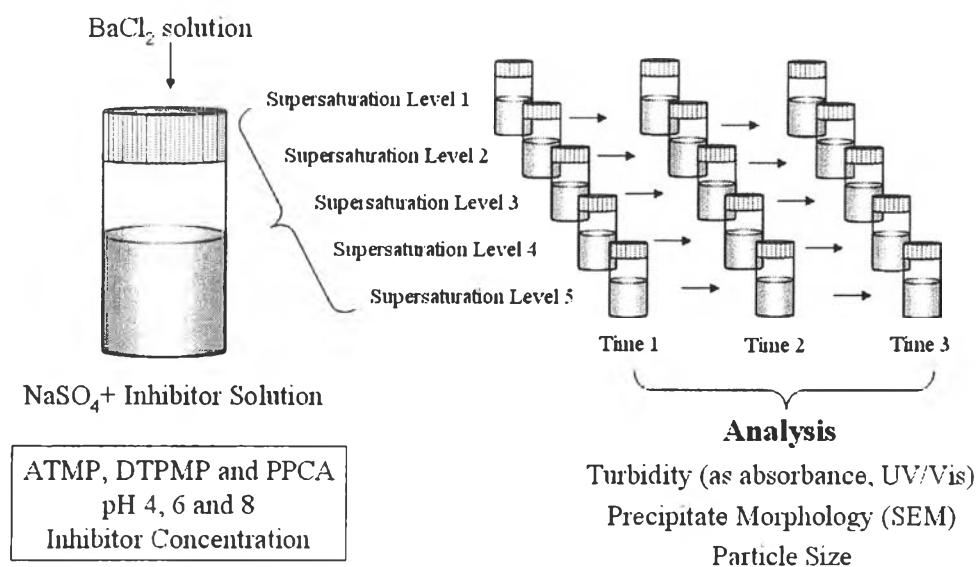
The induction times of inhibitor precipitation were determined using the apparatus as shown in Figure 3.5. Turbidity of the solution in terms of absorbance was monitored by circulating the solution through the quartz flow cell placed in a UV/Vis spectrophotometer (Varian, 300 Bio).



**Figure 3.5** Induction time determination apparatus.

### 3.2.7 Determination of Critical Supersaturation Ratio

Scale inhibition ( $\text{BaSO}_4$ ) experiments were carried out in 20 ml vials batch experiments as illustrated in Figure 3.6.  $\text{Na}_2\text{SO}_4$  solution was first mixed with the scale inhibitor solution. Afterwards, stock solution of  $\text{BaCl}_2$  was added in order to attain various supersaturation ratios. All vials were vigorously shaken for complete mixing. The solution turbidity (as absorbance of light at 250 nm) was determined at preestablished intervals. Critical supersaturation ratio or CSSR is a critical supersaturation ratio where after the turbidity increase steeply due to nucleation and growth of  $\text{BaSO}_4$  particles. Scale inhibition could be due to an effect on either nucleation rate and/or growth rate. The turbidity measurement alone cannot differentiate between these mechanisms and therefore we make no assumptions about which of these possibilities controlling the formation of precipitate in the solution. All procedures were performed at room temperature ( $25^\circ\text{C}$ ).



**Figure 3.6** Illustration of the procedure used to determine CSSR value for  $\text{BaSO}_4$  inhibition.

### 3.2.8 Particle Size Distribution Analysis

A Centrifugal Particle Size Distribution Analyzer (CAPA-500, Horiba Instruments Inc.) was utilized to determine the particle size distribution of the precipitates.

### 3.3 References

Browning, F. H. (1996) Precipitation and Dissolution of Calcium-Phosphonates for the Enhancement of Squeeze Lifetimes. Ph.D. Thesis, University of Michigan, Ann Arbor, USA.

Solutia (1998) Introductory Guide: Dequest Phosphonates. Missouri, USA.