CHAPTER VI
COMPARATIVE STUDY OF ATMP AND DTPMP
PHOSPHONATE SCALE INHIBITOR PRECIPITATION

6.1 Abstract

The precipitation of diethylenetriaminepenta methylene phosphonic acid (DTPMP) and aminotri methylenephosphonic acid (ATMP) with Ca ions has been studied and the effects of the pH, ionic strength and Mg ion on the inhibitor precipitation yield and inhibitor precipitate dissolution rate has been determined. The results shown that the precipitation yield increased with increasing in pH or ionic strength in the precipitation solution. The precipitation yield decreased with increasing in Mg ion concentration in solution. The percent of DTPMP mole precipitated from solution are on average 25% greater than that of ATMP at the same molar product of divalent cation to scale inhibitor. It was found that the solution pH is a significant parameter controlling the composition of inhibitor precipitates. The molar ratio of divalent cations to inhibitor in precipitates was found to increase with increasing in solution pH. The dissolution rate of inhibitor precipitate decreased significantly with increasing in molar ratio of divalent cation to inhibitor in precipitate. The dissolution rate of Ca-DTPMP precipitate is approximately five times faster than that of Ca-ATMP precipitate. The amount of inhibitor precipitate together with dissolution rate of inhibitor precipitate can be used as an indicator to compare lifetime of precipitation squeeze in different systems.

6.2 Introduction

The deployment of scale inhibitors using precipitation squeeze technique has proven to be an effective method to retain scale inhibitors in oilfield for inorganic scale control application. Success downhole treatment in many fields is attributed to the squeeze treatments using precipitation technique where scale inhibitors precipitate within the interstice of the formation rock. The treatments are carried out by squeezing (injecting) an aqueous inhibitor solution into a reservoir, the

inhibitor is then retained in the formation as a salt precipitate with divalent cations. Subsequent release of inhibitor into the produced water during production provides an inhibition of scales (Browning and Fogler, 1996).

DTPMP phosphonate scale inhibitor was used as a model scale inhibitor attempting to illustrate the scale inhibitor evaluation analysis for squeeze treatment. ATMP results obtained in the previous study were comparative compared. Phosphonate scale inhibitors, DTPMP and ATMP, common scale inhibitors used in the petroleum industry were selected as model scale inhibitor in this study. Fundamental studies on the effects of pH and Mg ion on DTPMP precipitation were conducted in the batch precipitation experiment similarly to ATMP research in Chapter IV. The dissolution rates of scale inhibitor precipitates together with scale inhibitor precipitate yield were used as indicators to compare lifetime of precipitation squeezes using two different scale inhibitors.

An increase in the squeeze lifetime is a key of the treatment in order to minimize the cost of the expensive chemicals, pumping cost and most importantly lost production. The duration of time that the inhibitor concentration in produce water remains above the effective concentration to prevent the scale formation is known as the squeeze lifetime. Factors governing the squeeze lifetime including the total quantity of inhibitor precipitation and dissolution rate of precipitated inhibitor were investigated in this study.

6.3 Materials and Methods

6.3.1 Materials

Commercial grade DTPMP (diethylenetriaminepenta methylene phosphonic acid) and ATMP (aminotri methylenephosphonic acid) were supplied by Solutia as aqueous solutions (50% w/w). The DTPMP molecule contains five active phosphonate groups, which forms five potential reacting sites for divalent cations while ATMP contains three active phosphonate groups. The chemical structures of these two inhibitors are shown in Figure 6.1. Analytical grade $CaCl_2.2H_2O$ and $MgCl_2.6H_2O$ used in the precipitating experiments were obtained from Fisher Scientific. Analytical grade NaCl was used in some experiments to determine the

effect of ionic strength. The stock solutions were prepared by diluting the inhibitor stock solution or dissolving $CaCl_2$, $MgCl_2$ and NaCl in deionized water. KOH and HCl obtained from Fisher Scientific were used to adjust the precipitating solution pH during the precipitating experiments.
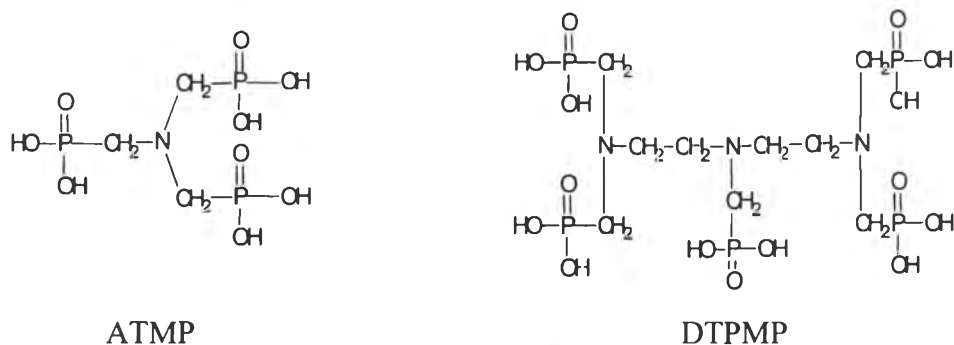

ATMP   DTPMP

Figure 6.1 Chemical structures of ATMP and DTPMP molecules.

6.3.2 Scale Inhibitor Precipitation

The deployment of scale inhibitors through the use of squeeze application was studied by determining the primary factor affecting the precipitation phosphonate scale inhibitors in batch experiments as shown in Figure 6.2. The effects of the pH, Mg ion and type of scale inhibitor were determined. A calculated amount of inhibitor solution was placed in a spherical flask, and stirred continuously by a magnetic stirrer. 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 the above solution, a calculated volume of $CaCl_2$ solution was added. Concentrated KOH and HCl were added drop wisely to maintain a desired solution pH. Then, the solution was left for three days in a closed flask at ambient temperature (25 °C) to allow complete 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. EDX was used to detect chloride in the precipitate. The removal of all Cl⁻ is necessary because it interferes with the determination of precipitate composition.

Mg precipitates with inhibitor were prepared with the same procedure as for Ca-Inhibitor, except that $MgCl_2$ solution was used in the precipitating solution instead of Ca. For Ca-Mg-Inhibitor precipitates, the precipitation procedures were the same as for Ca-inhibitor precipitation, except that $MgCl_2$ and inhibitor solutions were mixed together in a spherical flask before the addition of $CaCl_2$ solution. Ionic strength effect on precipitation of inhibitor was determined by adding NaCl into solution.
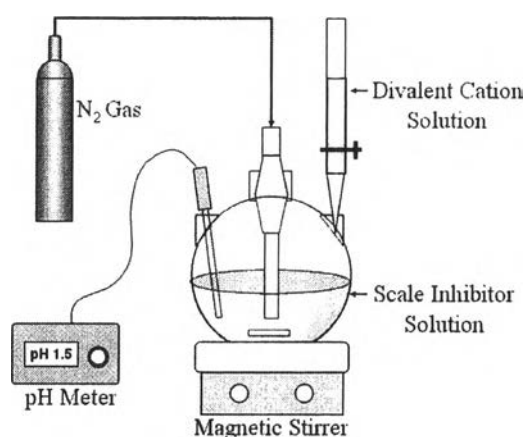

Figure 6.2 Scale inhibitor precipitation apparatus.

6.3.3 Determination of Scale Inhibitor Solubility

The effects of type of scale inhibitor, pH and Mg ions on the scale inhibitor solubility were determined as follows. The supernatant from section 6.3.2 after complete precipitation was filtered through 0.22 μm membrane to remove solid scale inhibitor precipitates. The supernatant was diluted with deionized water. The inhibitor concentration in the supernatant was determined using the Hach technique; 10 ml of solution was oxidized in the presence of persulfate under UV light for 10 min to produce orthophosphate. The molybdate blue was then mixed into the solution and the concentrations of inhibitor were determined colorimetrically using a UV spectrophotometer at wavelength 890 nm. The amount of the precipitated scale inhibitor was then calculated from the total concentration of inhibitor in the supernatants.

6.3.4 Characterization of Scale Inhibitor Precipitates

i. Composition Analysis

The ratio of Ca and Mg ions to scale inhibitor in the resulted scale inhibitor precipitates was determined using an Atomic Absorption Spectrometer (AAS) (Perkin-Elmer 3100) and Hach technique using a UV spectrometer (890 nm). Energy Dispersive X-ray Analyzer (EDX) was used to detect Cl^- interference in the precipitate and to confirm the ratio of Ca and Mg ions to scale inhibitor of precipitate samples.

ii. Morphology and Structure Analysis

The Scanning Electron Microscope (SEM) and X-ray Spectrometer were employed to determine for surface morphology at ambient conditions.

iii. Dissolution Rate Determination

The precipitate dissolution rates were determined using two types of reactor; a rotating disk and a differential reactor. The dissolution rates obtained from this experiment

6.4 Results and Discussion

The batch precipitation experiments in three systems, Ca-Inhibitor, combination of (Ca+Mg)-inhibitor and Mg-Inhibitor were conducted under various precipitating solution pH and at constant room temperature (25°C). The inhibitor concentration was maintained at 0.089 M in all the experiments.

6.4.1 Scale Inhibitor Solubility

The equilibrium supernatants from reacting solution were taken after approximately three days. The equilibrium inhibitor concentration was then measured and used to calculate the percent mole of inhibitor precipitated out from solution. The results are summarized in Table 6.1. DTPMP was used in experiments D1 to D12 while ATMP was used in experiments A1 to A9.

6.4.2   Effect of Solution pH

The scale inhibitors and divalent cation, Ca ions and Mg ions, concentrations were maintained at 0.089 M and 0.89 M respectively in all the experiments. That amount of precipitated inhibitor was found to increase as pH increased in both DTPMP and ATMP systems. For example, precipitation of scale inhibitors with Ca ions, DTPMP was precipitated 95% at pH 4 and 98% at pH 10. ATMP was precipitated 78% at pH 1.5 and 89% at pH 7. In Ca-Inhibitor system, no DTPMP precipitate was observed at pH 1.5 in contrast to that observed for ATMP. In Mg-Inhibitor system, no ATMP precipitates were formed at pH 1.5, 4 and 7 while DTPMP precipitates were formed at pH 6, 8 and 10. This suggests that Ca-DTPMP precipitations are highly sensitive to solution pH than Ca-ATMP while Mg-ATMP precipitations were found to sensitive to solution pH than Mg-DTPMP precipitations. Figure 6.3 shows a plot of the amount of inhibitor precipitated (mole percent) as a function of solution pH of two types of inhibitor with either Ca or Mg ions. At the same solution pH of 4 and any given cations, the amount of DTPMP precipitated is greater than that of ATMP.

6.4.3   Effect of Mg ions

The effect Mg ion on the precipitation of inhibitor was investigated in the presence of Ca in solution. The results from this study are shown in Figure 6.4. The concentration of inhibitor and Ca ion were maintained constant at 0.089 M and 0.89 M respectively in all experiments. The effluent of Mg ion on inhibitor precipitation was carried out by adding $MgCl_2$ into solution to obtain 1:1 Mg/Ca molar ratio in the final solution.

Table 6.1 Summary of inhibitor solubilities under different batch precipitating conditions.

	Precipitating Condition					Scale Inhibitor
	Solution pH	[Inhibitor] (M)	[Ca] (M)	[Mg] (M)	Ionic Strength (M)	Equlibrium Solubility (M)
D1	1.5	0.089	0.89		2.67	no precipitate formed
D2	4	0.089	0.89		2.67	0.0045
D3	6	0.089	0.89		2.67	0.0027
D4	8	0.089	0.89		2.67	0.0018
D5	10	0.089	0.89		2.67	0.0018
D6	4	0.089	0.89	0.89	5.34	0.0356
D7	6	0.089	0.89	0.89	5.34	0.0285
D8	8	0.089	0.89	0.89	5.34	0.0080
D9	10	0.089	0.89	0.89	5.34	0.0018
D10	4	0.089		0.89	2.67	no precipitate formed
D11	6	0.089		0.89	2.67	0.0703
D12	8	0.089		0.89	2.67	0.0231
D13	10	0.089		0.89	2.67	0.0045
A1	1.5	0.089	0.89		2.67	0.0196
A2	4	0.089	0.89		2.67	0.0116
A3	7	0.089	0.89		2.67	0.0098
A4	1.5	0.089	0.89	0.89	5.34	0.0516
A5	4	0.089	0.89	0.89	5.34	0.0356
A6	7	0.089	0.89	0.89	5.34	0.0338
A7	1.5	0.089		0.89	2.67	no precipitate formed
A8	4	0.089		0.89	2.67	no precipitate formed
A9	7	0.089		0.89	2.67	no precipitate formed

The amount of inhibitor precipitated decreased remarkably with an addition of Mg ions into solutions in both ATMP and DTPMP systems at all solution pHs The smaller amount of precipitated is due to the formation of Mg-inhibitor complex as discuss in ATMP studies in Chapter IV. Less Mg ions affect on Ca-DTPMP precipitation was observed at high solution pHs (pH 8 and pH 10). At pH 4, 95% DTMP was precipitated in the absence of Mg ions while in the presence of Mg ions only 60% DTPMP was precipitated; the difference in precipitation mass is approximately 35%. At pH 10, 98% DTMP was precipitated in the absence of Mg ions while 95% DTPMP precipitated in the presence of Mg ions, only 3% difference in precipitation mass was observed. A similar Mg ions effect was also observed for the precipitation of Ca-ATMP. This significant reduction of inhibitor precipitated especially at a low solution pH occurs if a significant amount of
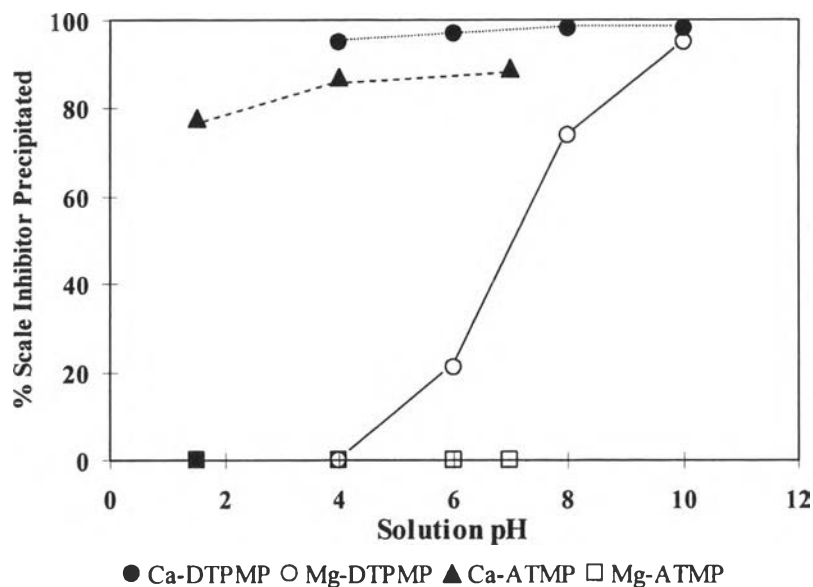
Figure 6.3 The amount of inhibitor precipitated as a function of solution pH of two types of inhibitors with Ca and Mg ions.
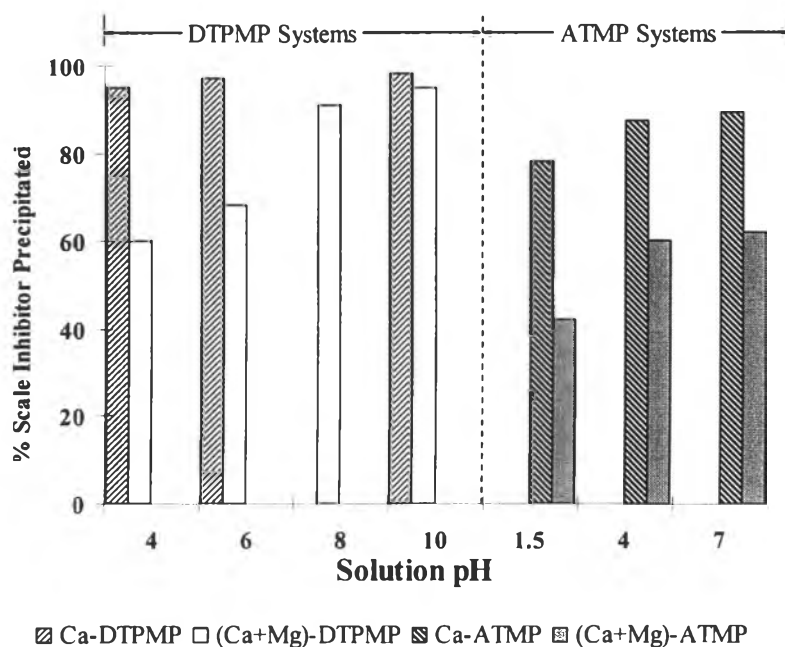

Figure 6.4 Effect of Mg ion on the amount of scale inhibitors precipitated under various solution pHs

magnesium mineral contains in formation material such as brucite $(Mg(OH)_2)$, epsomite $(MgSO_4.7H_2O)$, or magnesite $(MgCO_3)$. A lesser inhibitor precipitate will be retained in the reservoir and when the production resumes un-precipitated inhibitor will quickly sweep from the formation into a produced fluid. This will result in an inefficient use of the inhibitor and decreasing in a squeeze lifetime.

6.4.4 Precipitate Compositions

The compositions of DTPMP precipitates (expressed as total divalent cation to DTPMP molar ratio in precipitate) are shown in Figure 6.5. An increasing solution pH resulted in an increase in total divalent cations to DTPMP molar ratio in precipitates DTPMP precipitated at high pH contain greater amount of divalent cation as similar as that observed in the ATMP precipitation study.

The molar ratios of Ca to DTPMP in the precipitates were increased from 2.39 at pH 4 to 3.82 at pH 10. No step increasing of Ca to DTPMP molar ratio was found as in the Ca-ATMP study. In the Mg-DTPMP precipitation study, the molar ratios of Mg ions to DTPMP of the Mg-DTPMP precipitate was increased from 4.13 at pH 6 to 4.96 at pH 10. No Mg-DTPMP precipitate was formed at pH 1.5 and pH 4. At all pH, the molar ratio of Ca to DTPMP in the Ca-DTPMP precipitate is lower than that of Mg to DTPMP in the Mg-DTPMP precipitate.

The effect of Mg ion on Ca-DTPMP precipitation was studied by keeping the concentration of DTPMP and $CaCl_2$ constant at the previous values of 0.089 M and 0.89 M respectively and maintained 1:1 molar ratio of Ca to Mg in solution in all the experiments. The molar ratios of Ca and Mg to DTPMP in the Ca-Mg-DTPMP precipitates were determined at various solution pHs. For any given solution pH, the total molar ratio of divalent cations to DTPMP was found to fall below the molar ratio of Mg to DTPMP of the precipitate formed in the Mg-DTPMP experiments but above the molar ratios of Ca to DTPMP of the precipitate formed in the Ca-DTPMP study. The molar ratio of Ca to DTPMP is lower than that of Mg-DTPMP in (Ca+Mg)-DTPMP precipitates while at a very high pH (pH 10), the molar ratio of Mg to DTPMP in the precipitates is greater than that of Ca to DTPMP. The results indicate that DTPMP affinity for Ca is high at low solution pH environment, but as

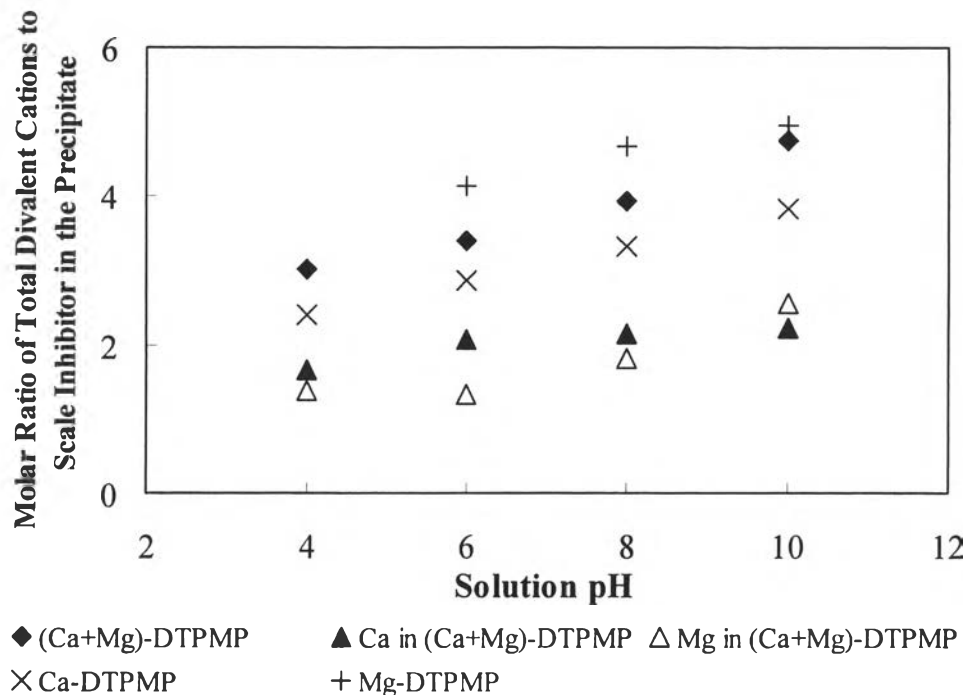the solution pH increased, there is a crossover point at which DTPMP preferentially binds with Mg ions.

Figure 6.5 Total divalent cations to DTPMP molar ratios in precipitates at various solution pHs.

6.4.5 Precipitate Morphologies

The morphologies of precipitates formed from DTPMP with different divalent cations were studied to further distinguish how the precipitating conditions can affect the resulting properties of DTPMP precipitate. The SEM micrographs of DTPMP precipitate are shown in Figure 6.6. The results show no significant difference in morphology of precipitates obtained from different precipitating solution pHs as seen in the case of ATMP. DTPMP particles obtained are similar in shape as powdered particles. The average DTPMP particle size can not be accurately measured. The DTPMP precipitates appear to be joined to other particles instead of single particles, consistent with the results reported by Graham.(Webb *et al.*, 1999) In comparison to ATMP precipitation, plate-like ATMP particles were observed at

pH 1.5. These particles were not joined but singular in appearance. In the presence of Mg ions, smaller ATMP particles were observed.

pH 4

pH 6

pH 8

pH10
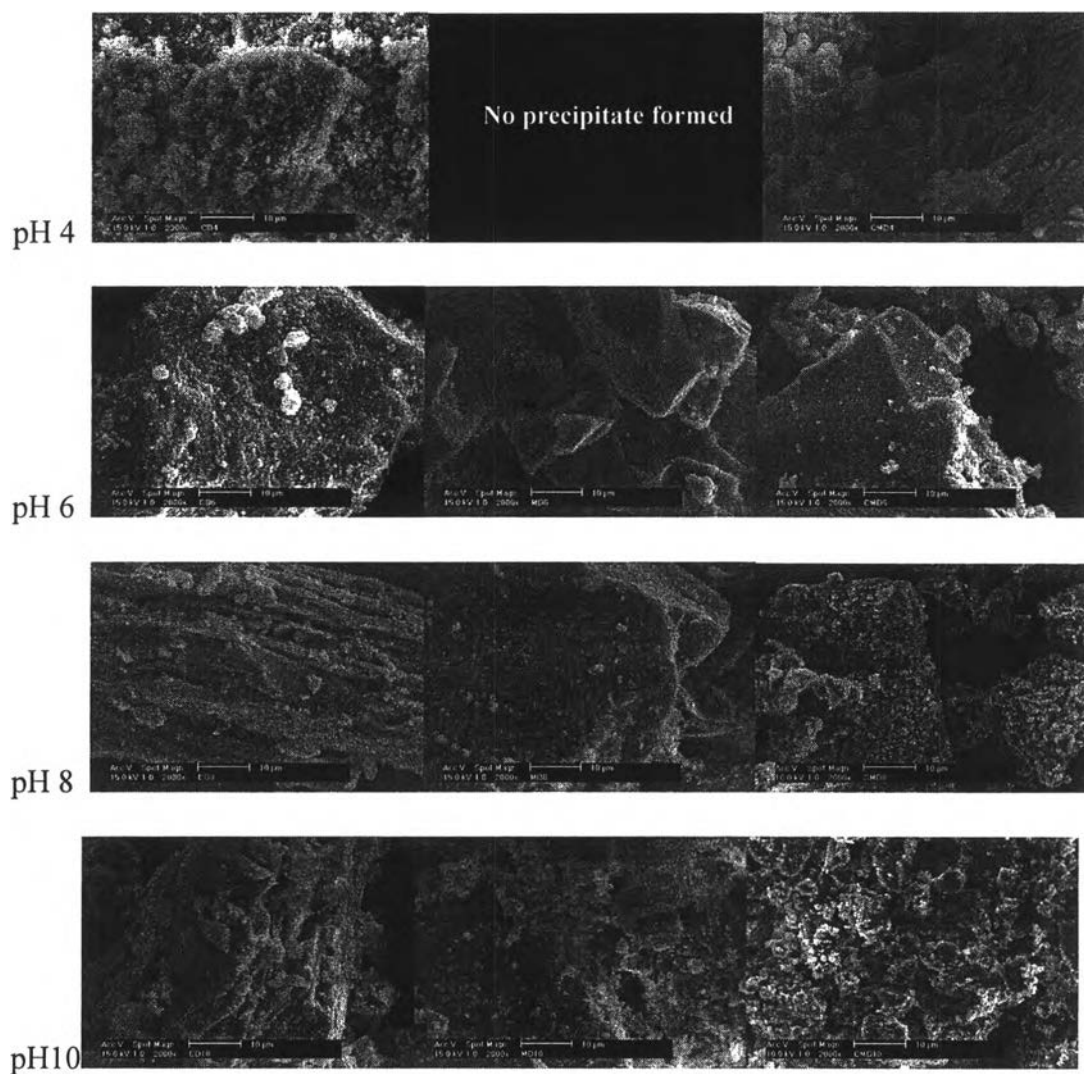
In the presence of

          Ca   Mg   Mixed Ca and Mg

Figure 6.6 Morphologies of the DTPMP with different divalent cations precipitates formed at various solution pHs.

6.4.6 Dissolution Rates

Batch dissolution experiments of the precipitates were carried out using a rotating disk reactor. A slow dissolution rate of inhibitor precipitate is desirable to

enhance lifetime of the squeeze treatment. The dissolution of rate of the precipitates obtained from the rotating disk was calculated from the number of inhibitor moles dissolved per unit pellet surface area per time. Figure 6.7 shows a comparison of the dissolution rates for Ca-inhibitor precipitates of both ATMP and DTPMP formed at different solution pH.
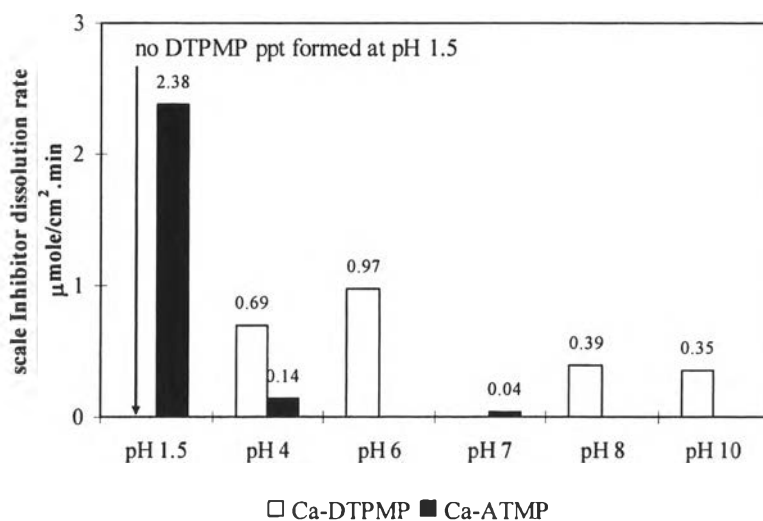

Figure 6.7 Dissolution rates of Ca-DTPMP and Ca-ATMP precipitates at various solution pHs.

DTPMP precipitates were found to have relatively slower dissolution rate than those of ATMP. For example, at pH 4, the dissolution rate of the Ca-DTPMP precipitate was about 5 times that of the Ca-ATMP precipitate. These results suggest that there is a potential of longer squeeze lifetime of Ca-ATMP system than that of Ca-DTPMP system at solution pH 4. Both scale inhibitor precipitates formed at a high solution pH dissolved slower than that formed at a low pH. 70% reduction of dissolution rate was observed for Ca-ATMP precipitates formed at pH 4 and 7 as compared to only 50% reduction of dissolution rate for Ca-DTPMP precipitates at pH 4 and 8. From the results, the molar ratios of Ca to ATMP in the Ca-ATMP precipitate show to be an important factor affecting the dissolution characteristic of the precipitate. The molar ratios of Ca to DTPMP in the DTPMP precipitates have the less effect on the precipitate dissolution rates.

6.5 Conclusions

i. The phosphonate scale inhibitor precipitation yield increased with increasing pH but decreased with increasing the Mg ion concentration in solution.

ii. The percentage of DTPMP precipitated from solution was found to be generally greater than that of ATMP for the same molar product of divalent cation to scale inhibitor.

iii. The composition of inhibitor precipitates is mainly governed by the solution pH. The molar ratio of divalent cations to inhibitor in precipitates increased with increasing solution pH.

iv. The dissolution rate of inhibitor precipitated decreased with increasing in molar ratio of divalent cation to inhibitor in precipitate. The dissolution rate of Ca-DTPMP precipitate obtained at pH 4 is approximately five times faster than that of Ca-ATMP precipitate obtained at the same pH.

v. The amount of inhibitor precipitated together with dissolution rate of inhibitor precipitate may be used as an indicator to predict the squeeze treatment lifetime. The results indicates that Ca-ATMP system has a longer squeeze lifetime than Ca-DTPMP systems.

6.6 References

Browning, F. H. and Fogler, H. S. (1996) Effect of precipitating conditions on the formation of calcium-HEDP precipitates. Langmuir, 12(21): 5231-5238.

Webb, P. J. C., Nistad, T. A., Knapstad, B., Ravenscroff, P. D. and Collins, I. R. (1999) Advantages of a new chemical delivery system for fractured and gravel-packed wells. SPE Production & Facilities, 14(3): 210-218.