

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Batch synthesis and characterization experiments

A systematic study was conducted in order to understand the effects of precipitation conditions on the precipitate properties. Two sets of the experiment were performed. The calcium to ATMP molar ratios in the precipitating solution were held at 1:1 and 10:1 while the pH of the precipitation solution were varied from 1.5-9.5. A summary of results is shown in Table 4.1.

Table 4.1 Summary of Batch synthesis and Characterization

Experimental conditions		Precipitate characteristics	
pH	Ca / ATMP molar ratio		Solubility, ppm
1.5	1:1	1:1	2936
1.5	10:1	1:1	2460
4.0	1:1	2:1	2356
4.0	10:1	3:1	790
4.5	1:1	2:1	1883
4.5	10:1	3:1	545
6.0	1:1	2:1	1394
6.0	10:1	4:1	483
7.0	1:1	2:1	45
7.0	10:1	4:1	462
9.0*	1:1	3:1	24
9.0	10:1	4:1	236
9.5*	1:1	3:1	18

* Precipitate formed after left approximately 3 days

4.1.1 Coupled effect of pH and Calcium/ATMP molar ratio of the precipitating solution on the resulting precipitate composition

The results shown in Table 4.1 demonstrated that the precipitating solution's pH and calcium/ATMP molar ratio both have a significant effect on the composition of resulting precipitates. At a molar ratio of calcium to ATMP 1:1, as the pH was increased from 1.5-9.5, the molar ratio of calcium/ATMP in the precipitates increased from 1: 1 to 3:1. This observations can be described that the solution equilibrium shifted as the pH increased resulting in the increment of the number of hydrogens deprotonated from each ATMP molecule, as shown in Figure 4.1.

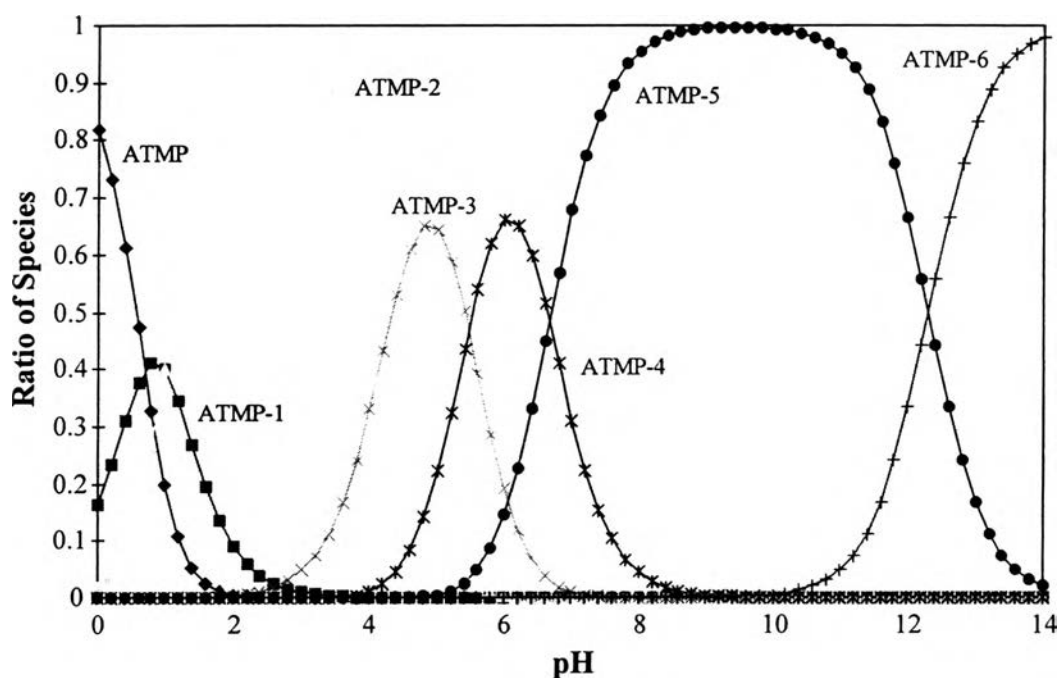


Figure 4.1 Deprotonation curve of ATMP.

At pH 1.5, the ATMP molecules are able to be deprotonated 1 to 2 hydrogens. This indicates that one calcium cation can potentially react with a ATMP molecule to form a 1:1 calcium-ATMP precipitate. While at pH 7.0, 4 to 5 hydrogens can deprotonate from each ATMP molecule, therefore, offers the potential for a 2:1 calcium-ATMP precipitate to form. This deprotonation,

consequently, enhanced the number of available sites for calcium to attach which, in turn, increased the calcium/ATMP molar ratio.

In addition, examining the results at pH 4.0, 6.0 and 9.0 closely, when the precipitating solution's calcium/ATMP molar ratio increased from 1:1 to 10:1, the calcium/ATMP molar ratio in precipitates changed from 2:1 to 3:1, 2:1 to 4:1 and 3:1 to 4:1, respectively. These phenomena occurred because the excess calcium has the ability to alter the chelation chemistry of the system and shift the solution equilibrium. As a result, the pK_a values were reduced. Consequently, it increased the amount of hydrogen deprotonation and the precipitate's calcium/ATMP molar ratio.

It is surprising that a 4:1 calcium to ATMP precipitate formed at a solution's molar ratio of 10:1 and pH value of 6.0 or greater. According to the structure of ATMP which contained 3 phosphate groups, three maximum calcium cation atoms can bond with one ATMP molecule by attacking hydrogen atoms on the phosphate groups and replacing the deprotonating species. However, because of the chelating property of calcium, it is possible for calcium cation to bond with the nitrogen in the center core of ATMP molecule.

4.1.2 Effect of the precipitating solution pH on the equilibrium solubility

It has been shown from the Table 4.1 that the precipitate formed at a precipitating pH of 1.5 has the highest value of equilibrium solubility while the precipitate formed at a precipitating pH of 9.5 has the lowest value of equilibrium solubility. It is apparent that the higher the precipitating solution's pH used for synthesizing the precipitate, the lower the equilibrium solubility the precipitate had. Eventhough the resulting precipitate's molar compositions were the same, but their equilibrium solubilities were significantly different.

Considering the 2:1 Calcium-ATMP precipitates which formed at pH 4.0, 4.5, 6.0 and 7.0 (precipitating molar ratio of 1:1), their values of equilibrium solubilities were 2356, 1883, 1394, and 45 ppm, respectively. The 3:1 and 4:1 precipitates also had the similar trends.

These significant differences in solubility are very important with respect to oil field applications since the equilibrium solubility limit can be used to indicate the rate at which the phosphonate scale inhibitors are released back into the production system and govern the squeeze lifetime.

4.2 Performance of precipitate in micromodel

4.2.1 Dissolution of the low solubility's precipitate

According to the experimental results obtained from the batch synthesis study, the precipitates formed at high solution's pH had low solubilities. Therefore, the further study of dissolution of these precipitate were conducted in the micromodel in order to examine the release process of the inhibitor from the porous media. The 3:1 Calcium/ATMP precipitate prepared at pH 9.0 and precipitating solution molar ratio of 1:1 was placed into the micromodel where it was left to shut in for approximately 48 hours, allowed the in-situ precipitation to occur. Then, the micromodel was eluted with deionized water which was adjusted pH values to 9.0 by using KOH solution. The pH 9.0 elution fluid was used in order to eliminate the possibility of the composition change in the precipitate due to the change of solution pH which was suggested by the results shown in Table 4.1.

The elution curve of the 3:1 precipitate illustrated in Figure 4.2 can be divided into two main regions. The release mechanisms in each region

can be determined by comparing the elution curve with the micromodel images shown in Figure 4.3.

Region 1: A sharp declining region : In this first region, the saturated calcium/ATMP solution initially in contact with the precipitate was swept from the micromodel resulting in the high ATMP concentration initially seen dropping rapidly in the elution curve. However, the precipitate was seemingly unaffected since dissolution or migration was undetectable.

Region 2: A extensive long tailing region: At this point, the elution curve reached the steady region. Dissolution of the precipitate in this region is slow and steady due to the low solubilities of the 3:1 precipitates. An examination of micromodel images after long period of time indicated that some precipitate had dissolved.

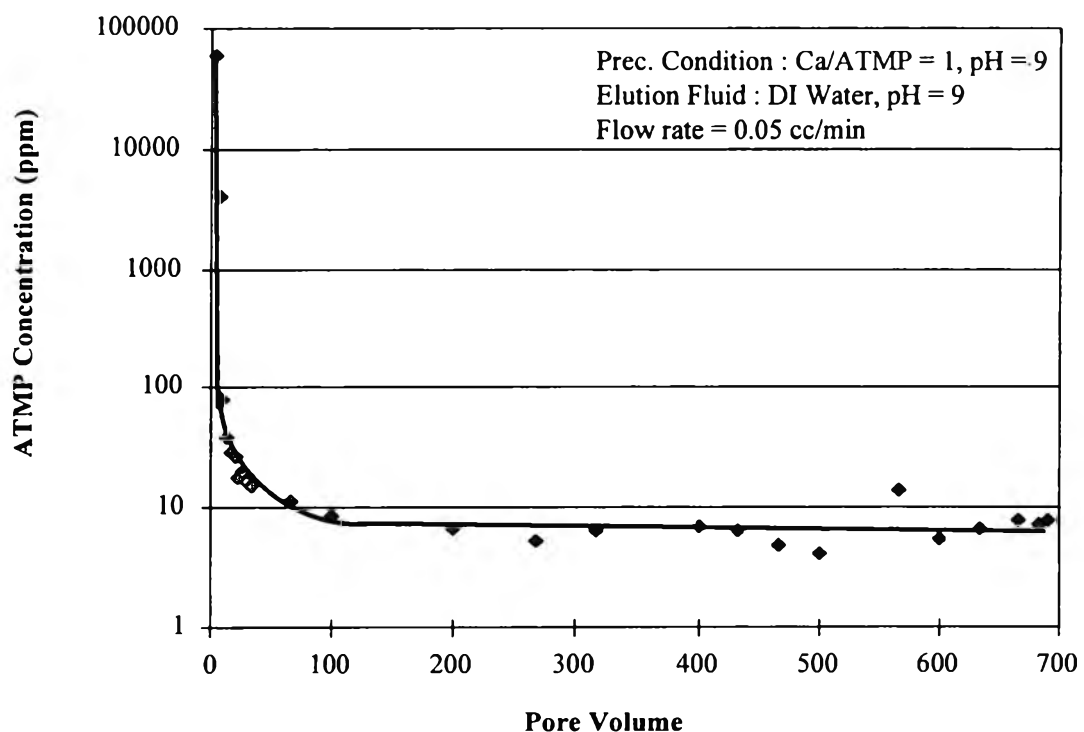


Figure 4.2 Elution curve resulting from dissolution of 3:1 Calcium-ATMP precipitate in micromodel.

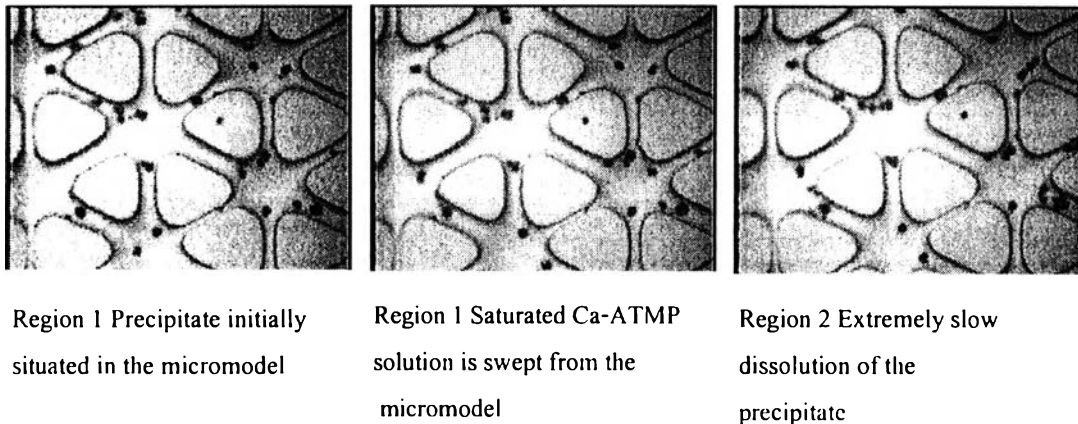


Fig. 4.3 Sequential release of 3:1 Ca-ATMP precipitate from a micromodel.

4.3 The effect of calcium concentration presented in elution fluid on the dissolution kinetics of precipitate

The observation in the previous works indicated that the increment of calcium cation in precipitating solution are able to change the chemical composition of the precipitate. The previous study of the precipitation performed with the phosphonates HEDP have shown that two distinct Ca-HEDP precipitates could be formed by varying the precipitating conditions (Browning and Fogler, 1996).

At pH of 1.5 and a 1:1 precipitating molar ratio, the 1:1 Ca-HDEP precipitate could be formed while the composition of the precipitate synthesized at pH of 6.0 and a precipitating molar ratio of 10:1, was 2:1 Ca/HEDP molar ratio. Therefore, both batch dissolution and micromodel experiments were performed to elucidate. Low the level of calcium concentration in dissolved fluid affect the dissolution of 1:1 Ca/phosphates precipitates.

Three types of dissolving solutions used were deionized water, 0.1 M CaCl₂ and 0.5 M CaCl₂. All batch dissolution experiments were performed at the solution's pH of 6.0. The solution's pH values were kept constant through the dissolution process in order to eliminate the effect of pH on the dissolution of the precipitates. The dissolution of 1:1 Calcium-HEDP and 1:1 Calcium-ATMP precipitates were observed. The phosphonates concentrations plotted as a function of time were shown in the Figure 4.4 and Figure 4.5. As can be seen from Figure 4.4 and 4.5, the presence of calcium ion in the dissolving solution could significantly reduce the equilibrium solubilities of both calcium-phosphate precipitates. These phenomena can be described by Le Chalelier Principle.



As the concentration of calcium increase, the reaction is forced to move to the left hand side of the reaction equation. As a result, the higher concentration of calcium in the solution, the less capacity of Ca-phosphonate precipitate dissolves.

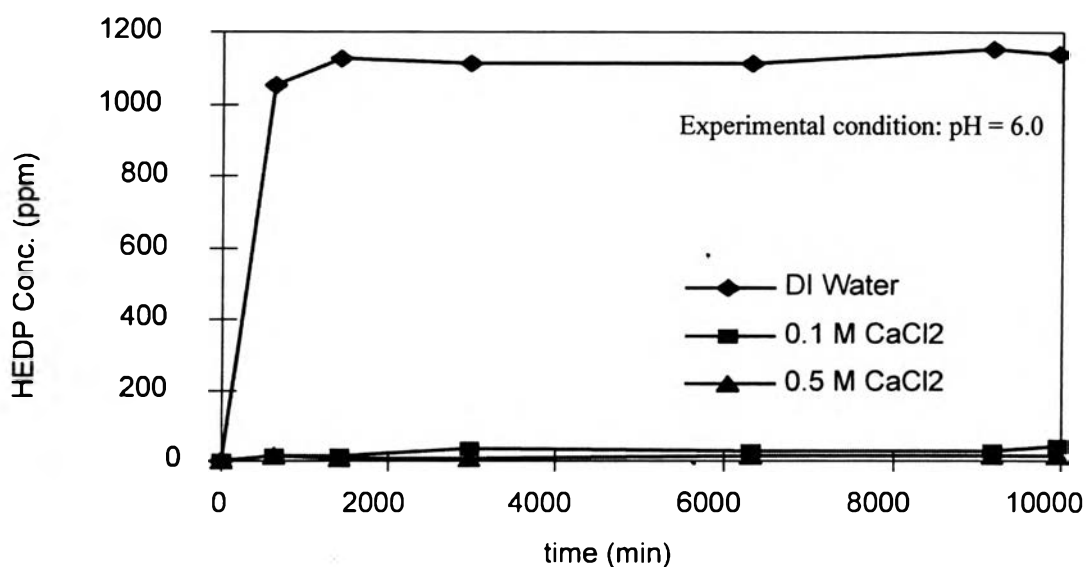


Figure 4.4 Effect of calcium concentration on dissolution of 1:1 Ca-HEDP precipitate.

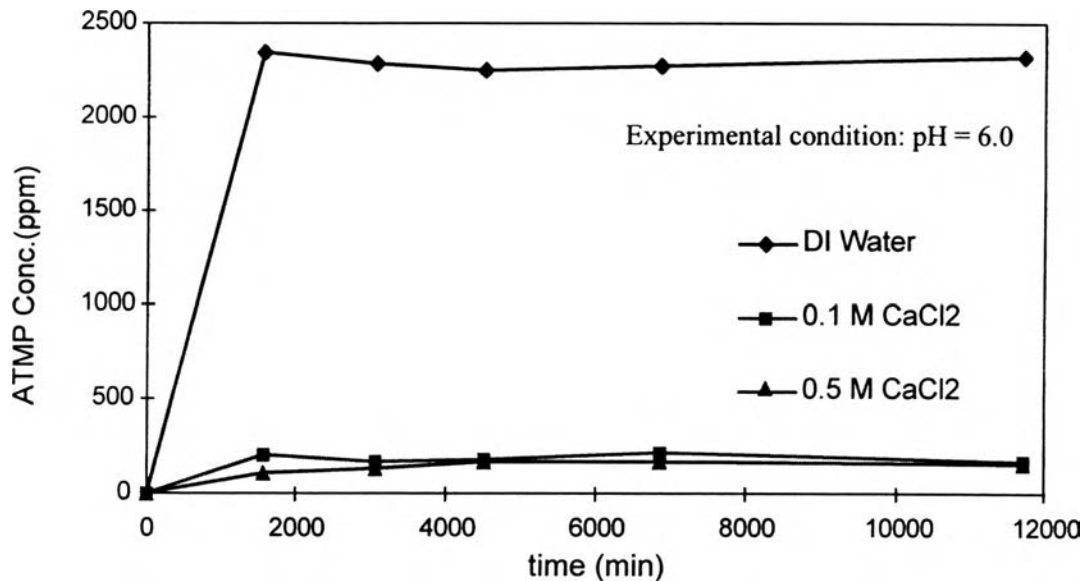


Figure 4.5 Effect of calcium concentration on dissolution of 1:1 Ca-ATMP precipitate.

4.3.2 Effect of calcium cation studied in micromodel experiments

To gain better understanding on how the calcium cation in the elution fluid affected the dissolution of Ca-phosphonate precipitates, the release of Ca-phosphonate precipitates from the micromodel was studied.

4.3.2.1 *1:1 Ca-HEDP precipitate.*

The elution curves (Figure 4.6), the normalised profile curves (Figure 4.7) and the time-lapse photographs (Figure 4.8) were comparatively studied in order to understand the release mechanisms of the precipitates from the micromodel. The curves were broken down into 3 regions which would be discussed as followed.

Region 1 : The release of the precipitate from the micromodel is dominated by the quick dissolution of long fibrous precipitate extending outward to the pore body resulting in the rapidly drop seen in the elution curve. Since the precipitate is easier dissolved in deionized water, the HEDP

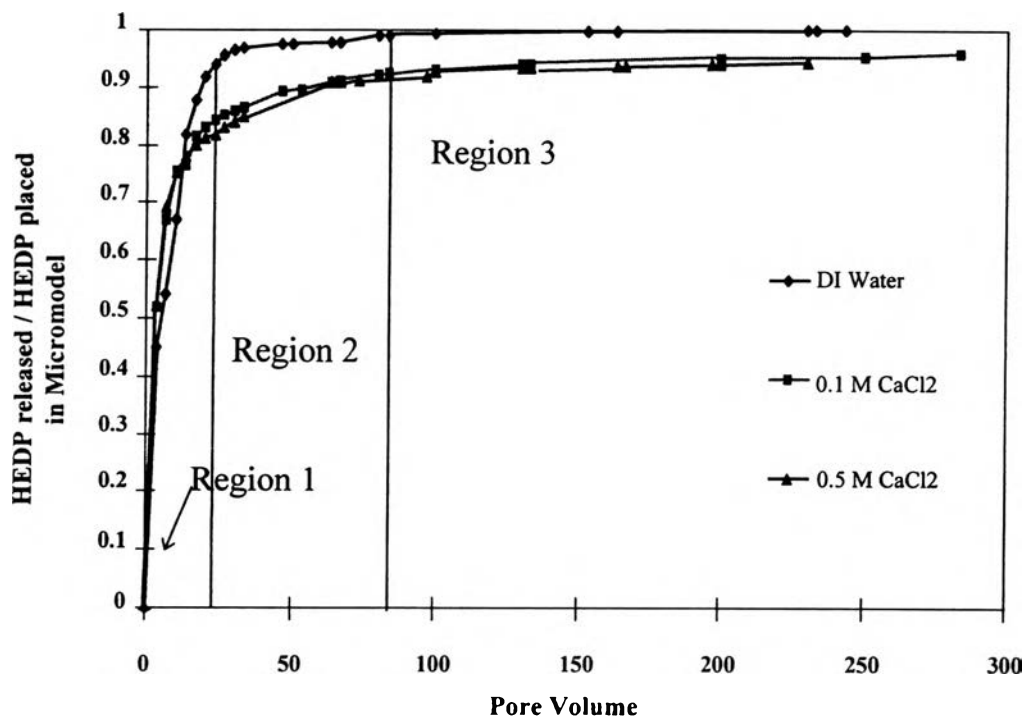


Figure 4.6 Effect of calcium concentration on the release of HEDP from the micromodel.

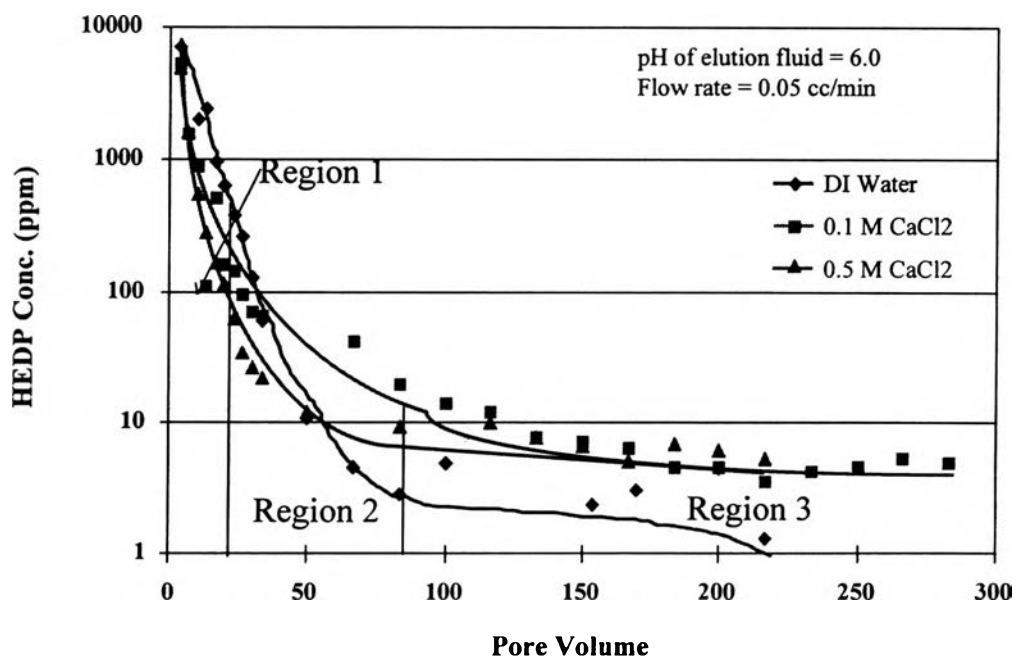


Figure 4.7 Effect of calcium concentration on the elution curves of 1:1 Ca-HEDP precipitates.

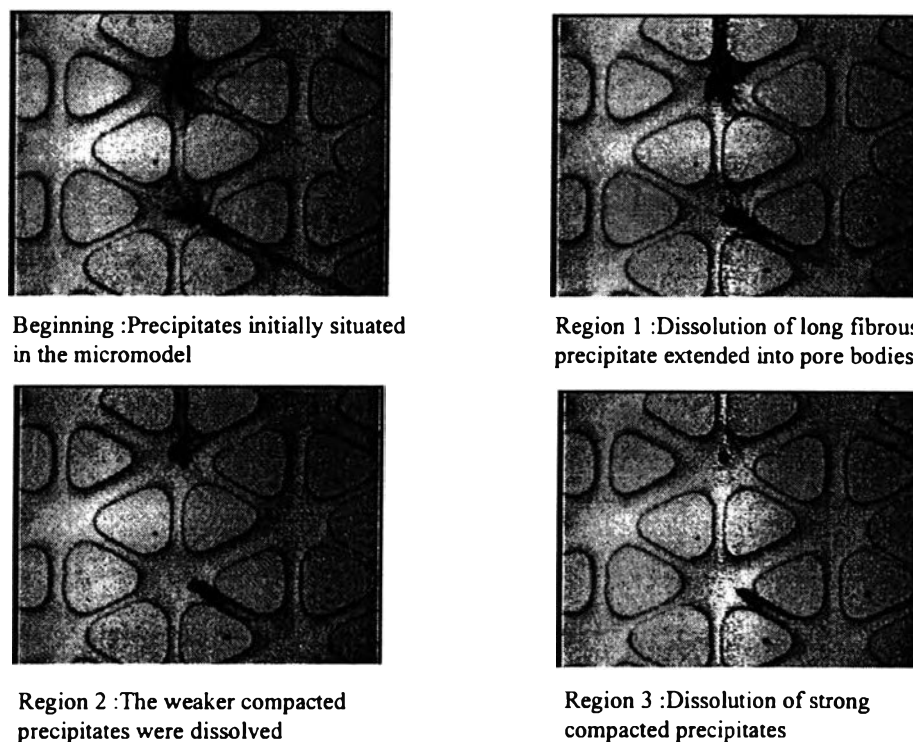


Figure 4.8 Sequential release of 1:1 Ca-HEDP precipitate from the micromodel for 0.5 M CaCl₂ elution fluid.

concentration level of the deionized water curve is higher than those of 0.1 M CaCl₂ and 0.5 M CaCl₂. The normalised release profiles of HEDP from the micromodel presented in Figure 4.6 support this result. During the first pore volume, most of all HEDP released into the effluent when deionized water was used as elution fluid while the less fraction of HEDP released in case of 0.1 M CaCl₂ and 0.5 M CaCl₂.

Region 2 : The compact precipitate is continuously dissolved as evident in the slow increase in the release profile curve. As a result, the elution curves are gradually declined. The concentration of HEDP in the deionized water curve fell below those of 0.1 M CaCl₂ and 0.5 M CaCl₂ due to the fact that most of Ca/HEDP precipitates were dissolved.

Region 3 : In this region, all the elution curve reached the steady long tailing region. The extremely small increment illustrated in the release profile is a result of the diffusion-controlled dissolution of the precipitate

densely plugged in the pore throat. The lower inhibitor concentration region seen in the deionized water curve caused by the depletion of Ca/HEDP precipitate. It was shown in the normalized release profile curve for the deionized water case that the precipitate was completely dissolved. In contrast, the curves of 0.1 M CaCl₂ and 0.5 M CaCl₂ stayed at the higher inhibitor concentration level. The fact contributed to this observation is that the solubilities of the precipitate in CaCl₂ solutions are lower than those in deionized water. Therefore, the precipitates were dissolved slower into the 0.1 M CaCl₂ and 0.5 M CaCl₂. Consequently, while the precipitate was completely dissolved into deionized water, some precipitates were still remained in the micromodel when the CaCl₂ solutions were used as the elution fluid. These remaining precipitates play the important role to extend the long tailing region of the elution curve. These observations have indicated the benefit of the presence of high concentration of calcium in the elution fluid to enhance the squeeze lifetime.

4.3.2.2. 1:1 Ca-ATMP precipitate

The similar experiments conducted with 1:1 Ca/ATMP precipitates gave the comparable results. The elution curves (Figure 4.9) and the normalized release profile curves (Figure 4.10) can be divided into four regions. By comparing these curve with the micromodel images (Figure 4.11), the release mechanisms in each region could be described as follows.

Region 1 : The short flat region of high ATMP concentration following by sharp decline region seen in the beginning portion of the elution curve was due to the fact that the saturated Ca-ATMP solution initially in contact with the precipitate was swept from the micromodel. The normalized release profile has indicated that small portion of the inhibitor was released.

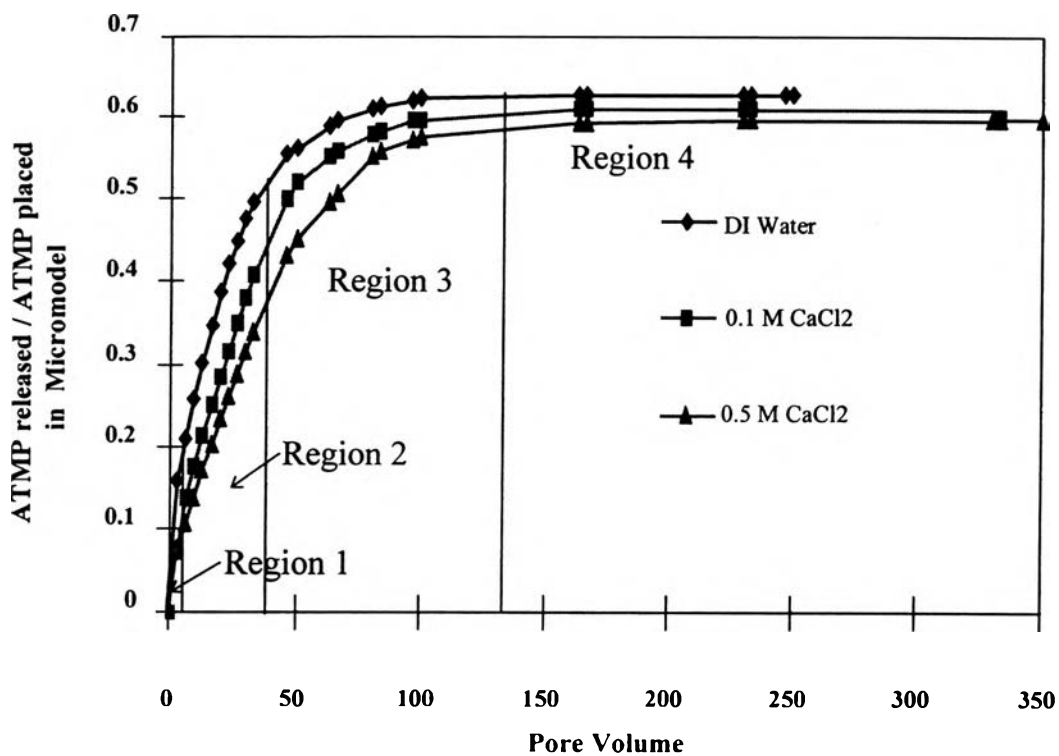


Figure 4.9 Effect of calcium concentration on the release of 1:1 Ca-ATMP precipitate from the micromodel.

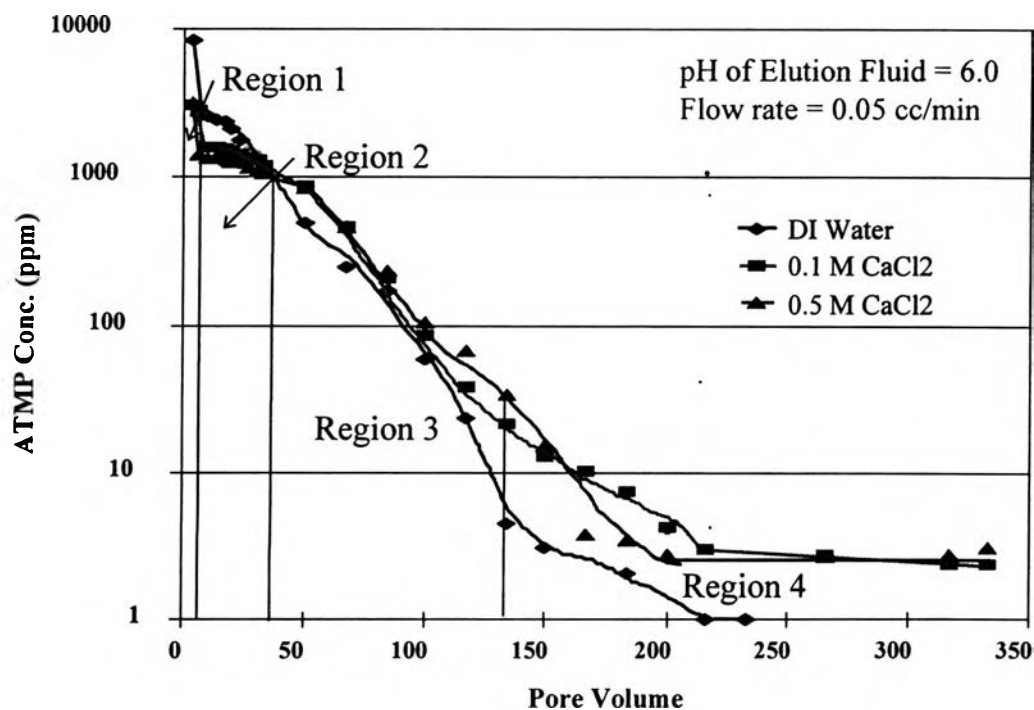


Figure 4.10 Effect of calcium concentration on the elution curves of 1:1 Ca-ATMP precipitates.

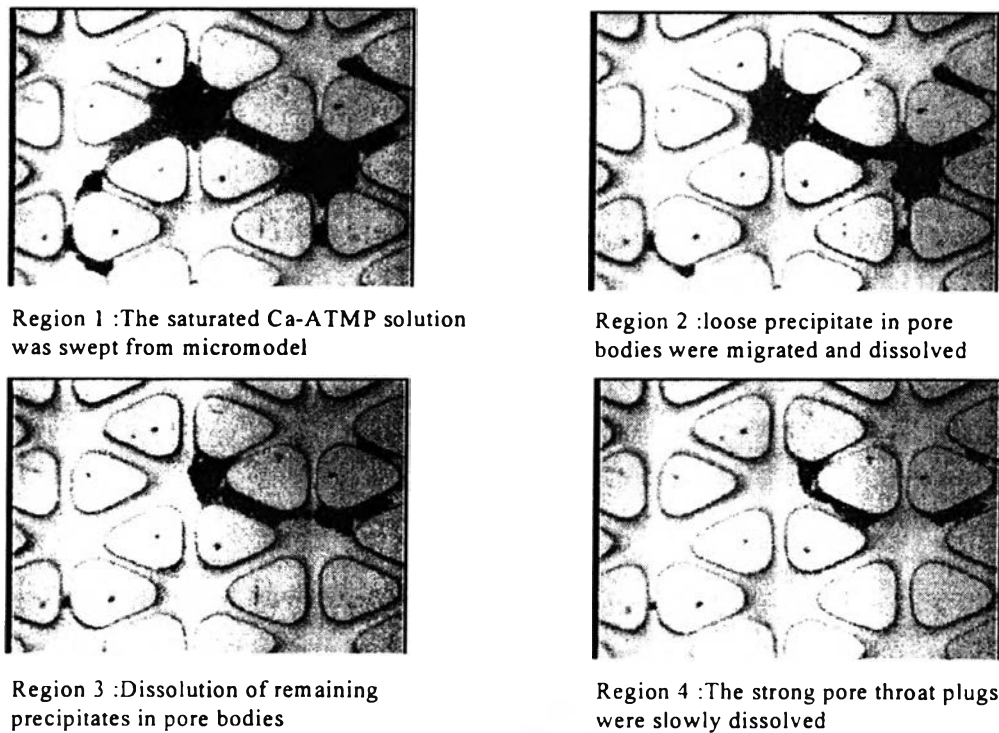


Figure 4.11 Sequential release of 1:1 Ca-ATMP precipitate from micromodel for 0.1 M CaCl_2 elution fluid.

Region 2 : Examination of the normalized release profile illustrated that a main portion of the inhibitor released from the micromodel in this region. These phenomena can be described by the dissolution and migration of the precipitate loosely packed in pore bodies. Similar to those observed with Ca/HEDP precipitate, the inhibitor concentration of the deionized water curve is higher than those of the 0.1 M CaCl_2 and 0.5 M CaCl_2 . It has verified the effect of calcium cation in the elution fluid on the dissolution of calcium/phosphonate precipitate.

Region 3 : In this region, the normalized ATMP release curve was gradually increased since the remaining precipitates in pore bodies were dissolved. It was corresponded to the more gradually declining region in the elution curves. The deionized water curve showed the lower ATMP

concentration level than 0.1 M CaCl₂ and 0.5 M CaCl₂ since the most of the precipitate was dissolved in deionized water as evident in the normalized release curves.

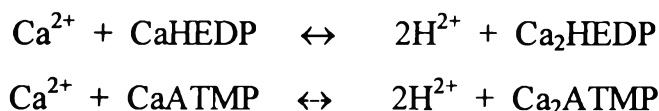
Region 4 : From the elution curve, the ATMP concentration level of deionized water curve dropped below those of 0.1 M CaCl₂ and 0.5 M CaCl₂. The normalized release profile curves showed that the larger portion of ATMP was releases into deionized water. These led to the falling of the inhibitor concentration level seen in the elution curve. The fact that the compact precipitates plugged in the pore throat were slowly dissolved contributed to the steady long tailing region seen in the end of this region. Similar to the observation found with Ca-HEDP precipitates, the CaCl₂ solutions curves stayed at the higher level of inhibitor concentration. These phenomena reconfirmed the ability of the calcium cation contained in the elution fluid to promote the squeeze lifetime.

4.4. Comparison between batch dissolution and micromodel experiments

Since the curves obtained from the micromodel experiments didn't show the drastic reduction of the inhibitor concentration due to the addition of calcium cation into the elution fluid as those found in the batch dissolution experiments, the addition experiments were conducted to verify this point.

After the dissolution curve reached the plateau region, the precipitates remaining in the beaker of batch dissolution experiments were recharacterized. The molar ratio of calcium to phosphonate of the recovered precipitates for both HEDP and ATMP phosphonates were changed from 1:1 to 2:1. This phenomenon is not unexpected since the transition from formation of a 1:1

precipitate to a 2:1 precipitate has been found in the previous work. (Browning and Fogler, 1996). This finding can be clearly explained by the following chemical equilibrium reactions:



It is apparent an increase in the calcium concentration will drive the equilibrium reaction to favor the formation transition from the 1:1 precipitate to the 2:1 precipitate. Consequently, the equilibrium solubility that had been observed dropped to the value comparable to the equilibrium solubility of 2:1 precipitate.

However, these tremendous differences in the inhibitor concentration had not found in the micromodel experiments. The time-lapse photograph observed through the micromodel demonstrated that the 1:1 precipitate did not transform to the 2:1 precipitate during the dissolution process. The possible reason was, since the dissolution process was dynamic, that the 1:1 precipitate did not have enough retention time to react with calcium cation and reach the equilibrium favor to the formation of 2:1 precipitate. Although the transformation from 1:1 precipitate to 2:1 precipitate did not occur, the increase of calcium concentration in the elution fluid affected the dissolution of the precipitate and extended the long tailing region of the elution curve. This result was an enhanced treatment with longer lifetime. Hence, the oil producers were able to obtain the desirable squeeze lifetime by adding the calcium cation into the elution fluid.