CHAPTER IV
RESULTS AND DISCUSSION

This thesis was divided into three main experimental sections. First section concerned with synthesis and characterization of 1:1 and 2:1 Ca^{2+}/HEDP precipitates and transformation of the Ca^{2+}/HEDP precipitates. Second section was to determine the dissolution kinetics of both the 1:1 and 2:1 Ca^{2+}/HEDP precipitates. Last section was to evaluate the performance of these precipitates in the micromodel which simulates the porous media. The experiment data are shown in Appendix.

4.1 Batch Synthesis and Characterization of Ca^{2+}/HEDP Precipitates

4.1.1 Synthesis of Ca^{2+}/HEDP Precipitates

This study was conducted to reproduce Ca^{2+}/HEDP precipitates described by the previous results. Two different batch experiments were performed for the synthesis of 1:1 and 2:1 Ca^{2+}/HEDP precipitates at molar product of 0.005 M^2. First batch experiment was conducted at pH = 2.0 which produced a 1:1 Ca^{2+}/HEDP precipitate. The second batch experiment was conducted at pH = 6.0 for the synthesis of a 2:1 Ca^{2+}/HEDP precipitate. This is a reproduction of the work conducted by Browning (1996) as shown in Figure 4.1.

At pH 2, the Ca^{2+}/HEDP precipitate having a molar ratio of 1:1 was formed. One calcium cation attached to one active phosphate group in HEDP to form the precipitate. The solubility product, K_{sp}, of this precipitate is approximately 3.02E-08 $(mol/l)^2$. While at pH 6, a Ca^{2+}/HEDP precipitate having a molar ratio of 2:1 was formed. Two calcium cations atoms react with one HEDP molecule to form the precipitate due to the effect of high pH

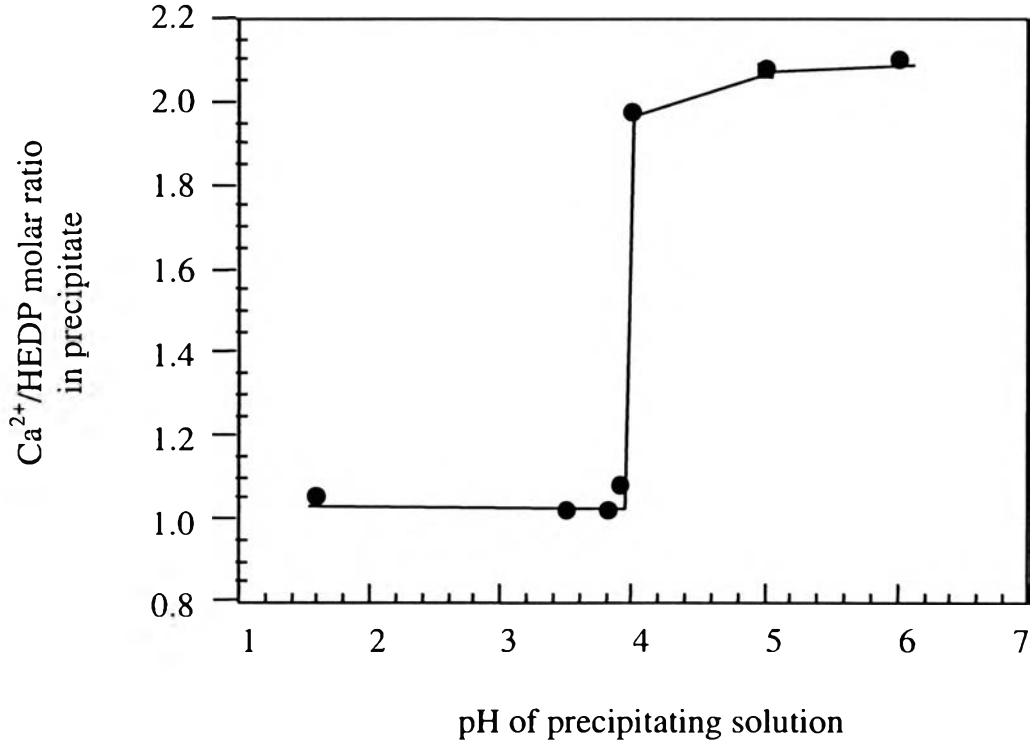
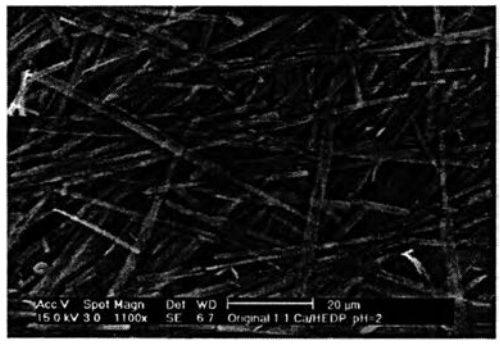


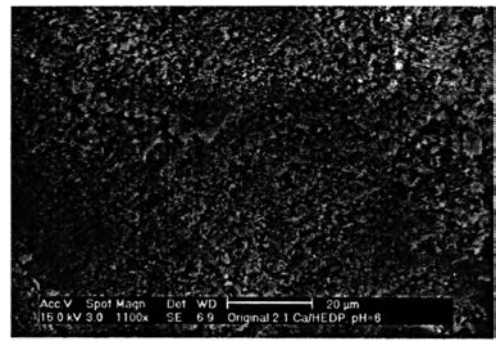
Figure 4.1 Effect of solution pH on Ca^{2+}/HEDP molar ratio of precipitate (Browning, 1996)

causing the HEDP molecule had the greater deprotonation, leaving more reaction sites for the calcium molecule to bond. The value of K_{sp} is approximately 8.12E-12 $(mol/l)^3$. The morphologies of these two precipitates are spindle particle and spherical particle, respectively, which are depicted in Figure 4.2.

The crystalline form of a 1:1 Ca^{2+}/HEDP precipitate is clearly seen in the form of a spindle shape whereas a 2:1 Ca^{2+}/HEDP precipitate is amorphous as shown in Figure 4.2. The X-Ray Diffraction (XRD) patterns of these precipitates again reconfirm that the 1:1 precipitate is crystalline and the 2:1 precipitate is amorphous as shown in Figure 4.3.



1:1 Ca^{2+}/HEDP precipitates, pH = 2



2:1 Ca^{2+}/HEDP Precipitates, pH = 6

Figure 4.2 Morphologies of 1:1 and 2:1 Ca^{2+}/HEDP precipitates synthesized at pH of 2 and 6, respectively

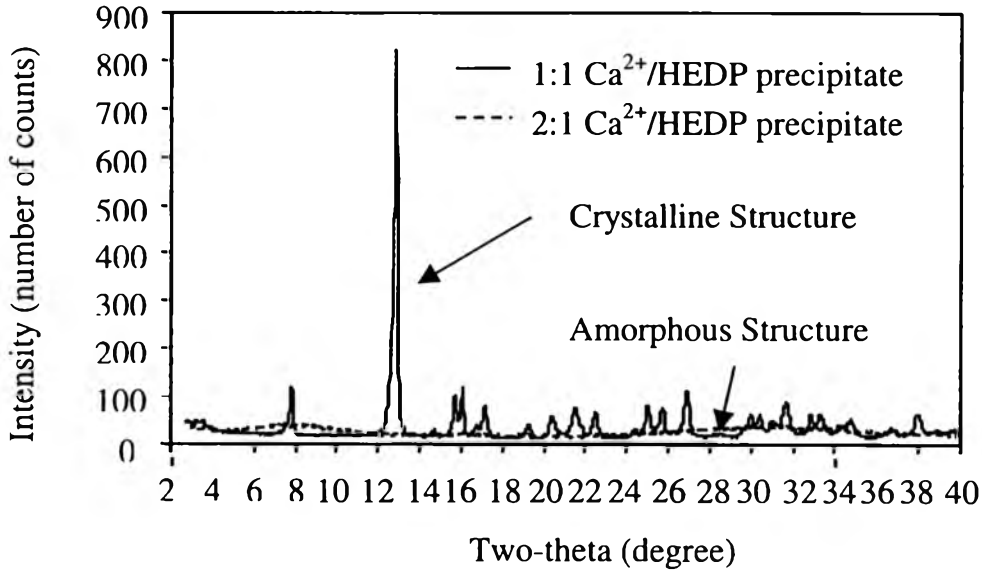


Figure 4.3 XRD patterns of two precipitates having 1:1 and 2:1 Ca^{2+} to HEDP ratios

4.1.2 Transformation of Ca^{2+}/HEDP Precipitates

Transformation of the precipitate depends on the pH of the solution and the type of the precipitate. The results of the previous study conducted by Browning (1996) shows that precipitate morphology depends on pH and the

Ca^{2+}/HEDP molar ratio of the solution. It has been found that a solution pH=2.0, the precipitate has 1:1 molar ratio of Ca^{2+} to HEDP, although at pH=6.0, the precipitate has molar ratio of 2:1. In order to see the transformation of the 1:1 precipitate to the 2:1 precipitate, the pH of precipitate solution was changed from a low pH of 2.0 to a high pH of 6.0. It was found that the spindle Ca^{2+}/HEDP precipitate was transformed to spherical particles. The transformation curve shown in Figure 4.4 reveals that the 1:1 Ca^{2+}/HEDP precipitate is completely transformed to the 2:1 Ca^{2+}/HEDP precipitate after 10 minutes.

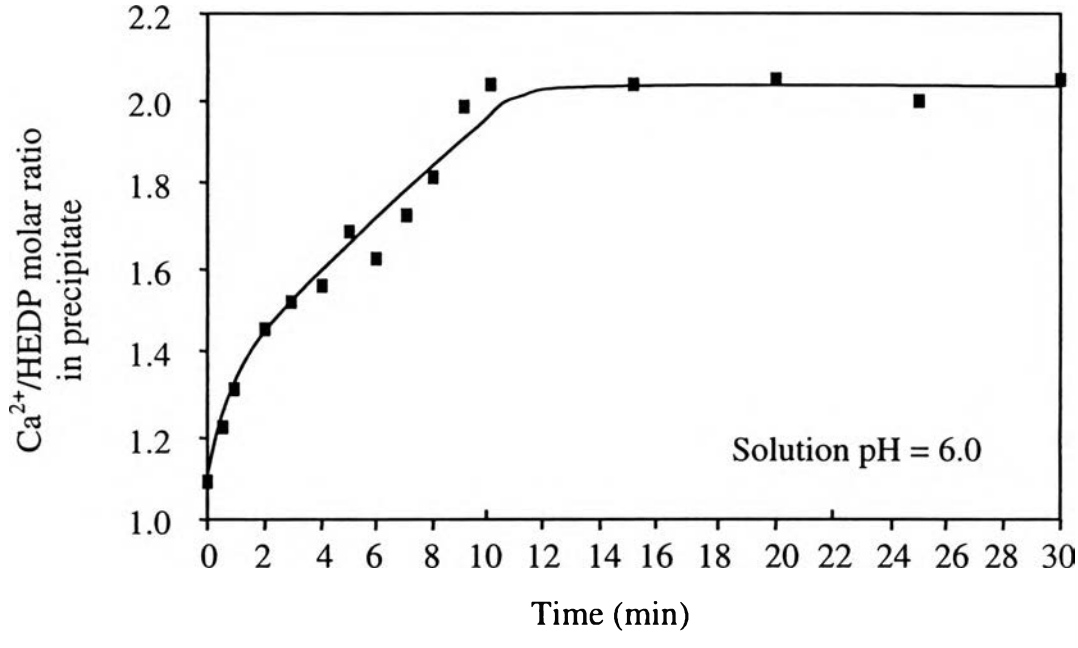


Figure 4.4 Ca^{2+}/HEDP molar ratio in precipitate as a function of time during transformation from 1:1 to 2:1 Ca^{2+}/HEDP precipitate at the solution pH = 6.0

As can be seen from Figure 4.5, the transformation of the 2:1 Ca^{2+}/HEDP precipitate to the 1:1 Ca^{2+}/HEDP precipitate occurs when the pH of the solution is changed from 6.0 to 2.0. This transformation phenomena

was clearly confirmed the observation of the morphology change from the spherical particle to long spindle particles as be desorbed latter in the next section. Comparing Figures 4.4 and 4.5, one can observe that the transformation of 2:1 Ca^{2+}/HEDP precipitate to 1:1 Ca^{2+}/HEDP precipitate is much slower than the transformation of 1:1 Ca^{2+}/HEDP precipitate to 2:1 Ca^{2+}/HEDP precipitate.

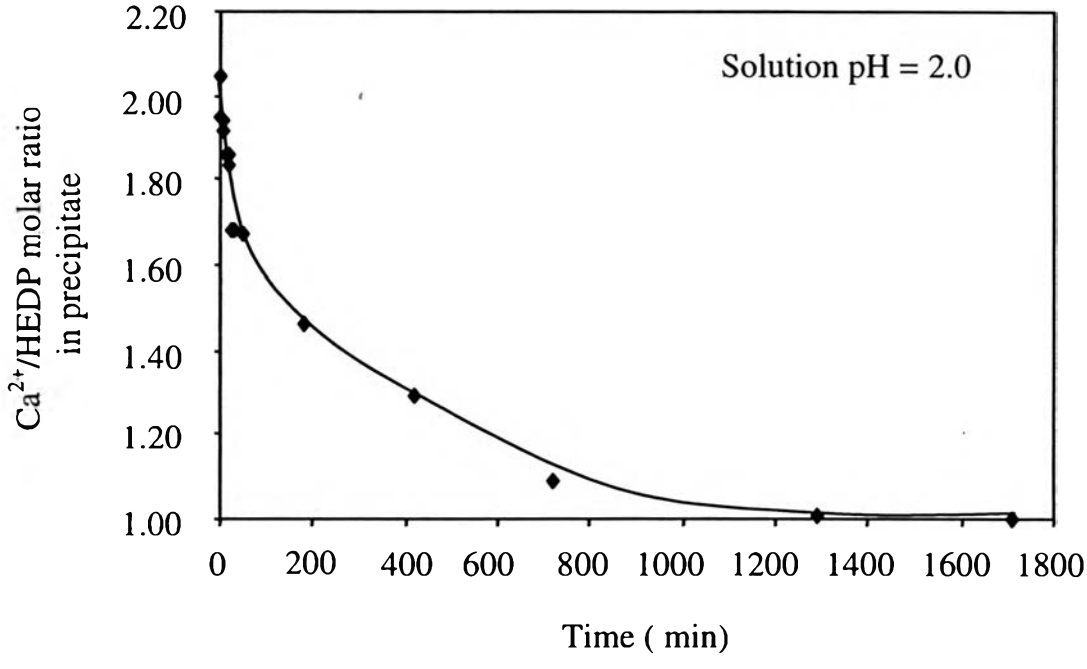
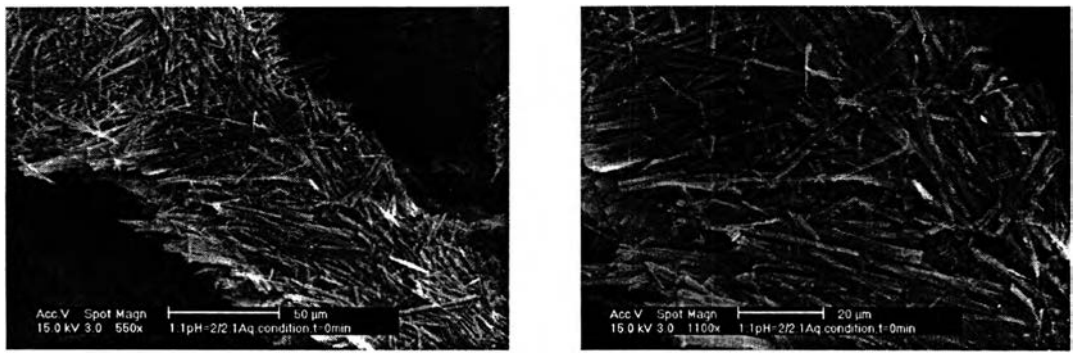


Figure 4.5 Ca^{2+}/HEDP molar ratio in precipitate as a function of time during transformation from 2:1 to 1:1 Ca^{2+}/HEDP precipitate

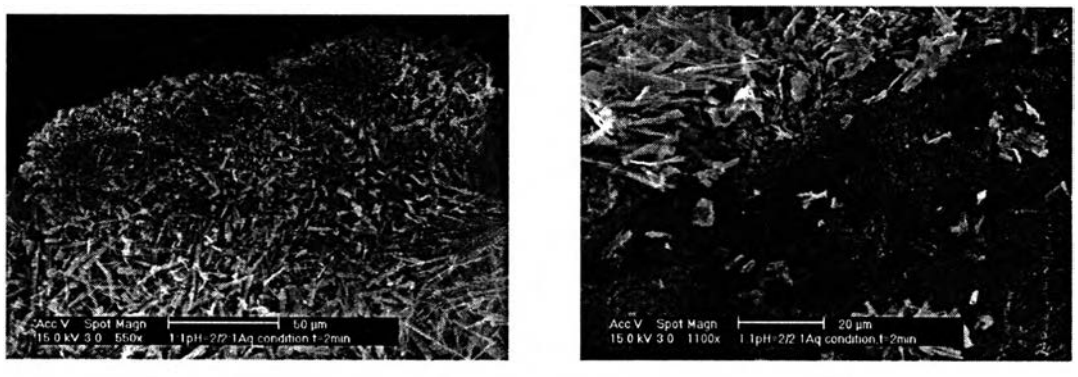
4.1.3 Changes in Morphology during Transformation of Precipitates

The morphologies of both 1:1 and 2:1 transformed Ca^{2+}/HEDP precipitates during transformation were studied by using Scanning Electron Microscope (SEM). Figure 4.6 shows the initially spindle-shaped precipitate during the first 2 minutes after let the transformation to occur. The 1:1 Ca^{2+}/HEDP precipitate

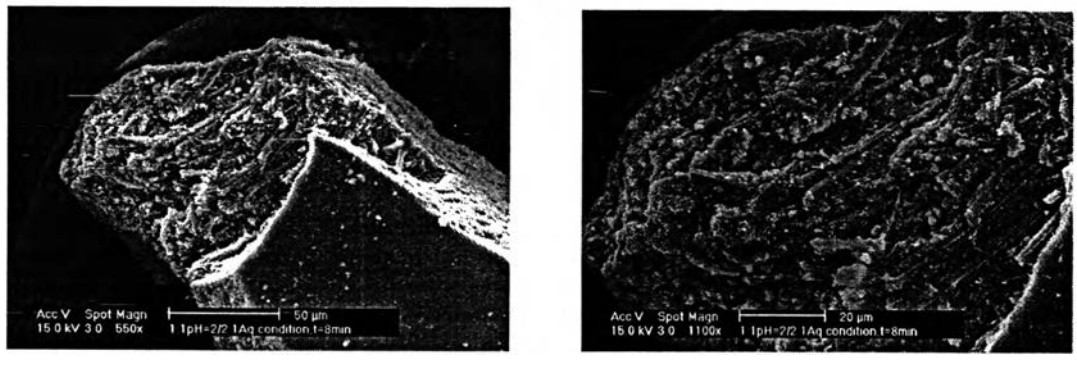
began to slightly transform its morphology at the edge and then the 2:1 saturated Ca^{2+}/HEDP solution diffused through internal surfaces of the precipitate. The spindle particles were then completely transformed to the spherical particles within only 20 minutes.



550x **0 minute** 1100x

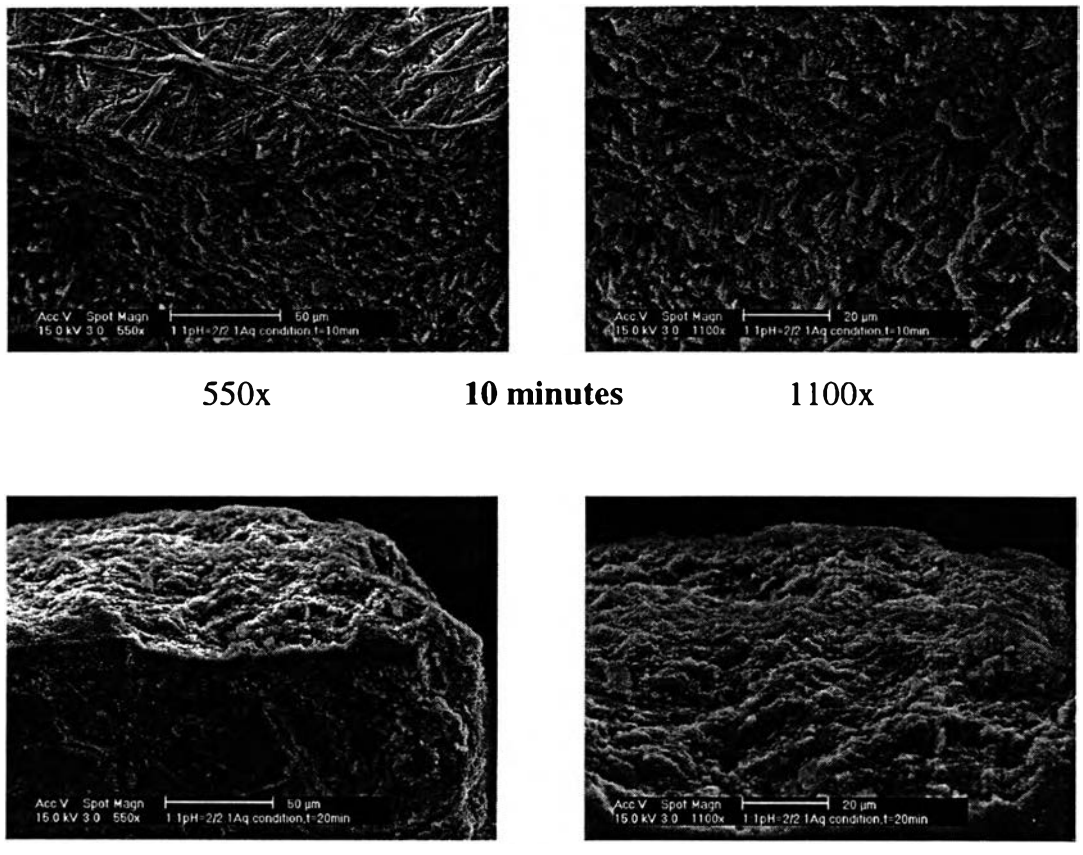


550x **2 minutes** 1100x



550x **8 minutes** 1100x

Figure 4.6 SEM pictures of the precipitate during transformation from 1:1 to 2:1 Ca^{2+}/HEDP molar ratio

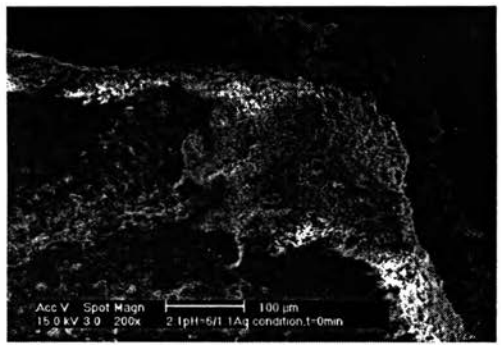


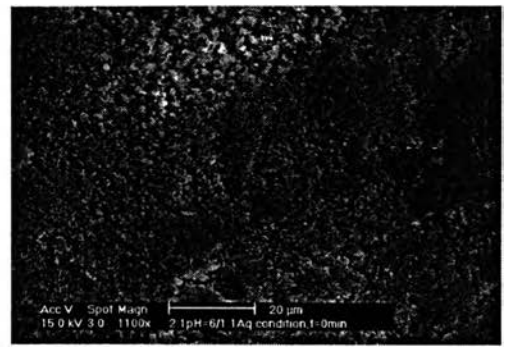
550x **10 minutes** 1100x

550x **20 minutes** 1100x

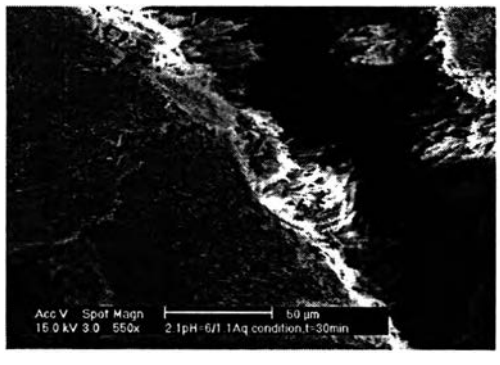
Figure 4.6 - continued.

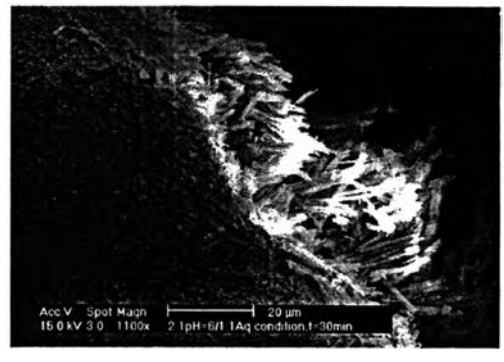
From Figure 4.7, the spherical-shaped solid of 2:1 Ca^{2+}/HEDP precipitate are partly transformed to the spindle-shaped solid of 1:1 Ca^{2+}/HEDP precipitate at the edge after 30 minutes. Then, it has been clearly seen that the 2:1 Ca^{2+}/HEDP precipitate was mostly transformed to the 1:1 precipitate at time 420 minutes and finally the complete transformation from the spherical particles to the spindle particles appeared when the time passed through 1,710 minutes.



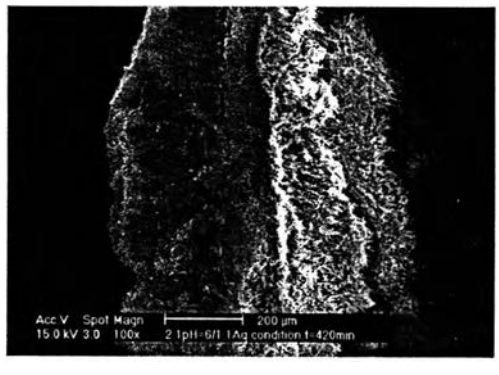


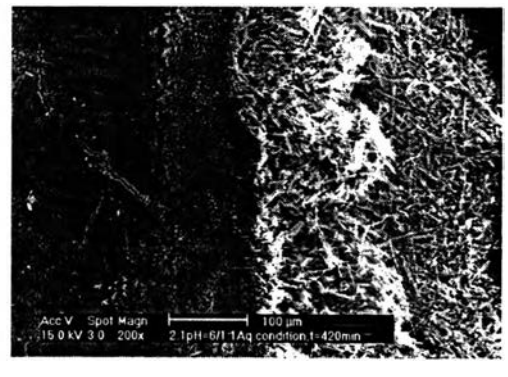
200x **0 minute** 1100x





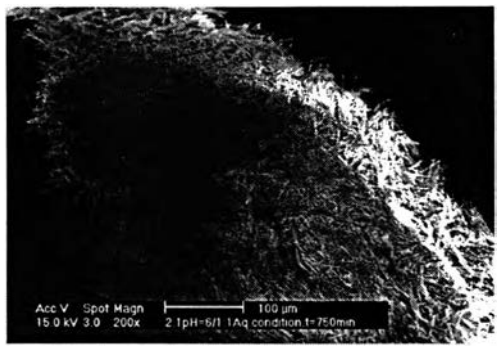
550x **30 minutes** 1100x



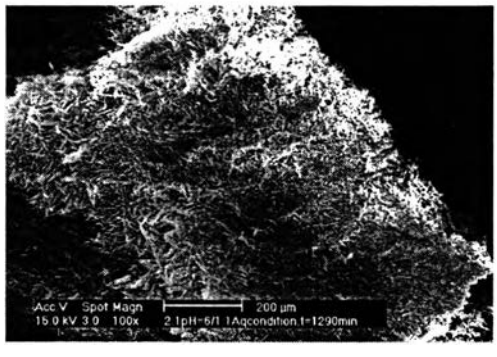


100x **420 minutes** 200x

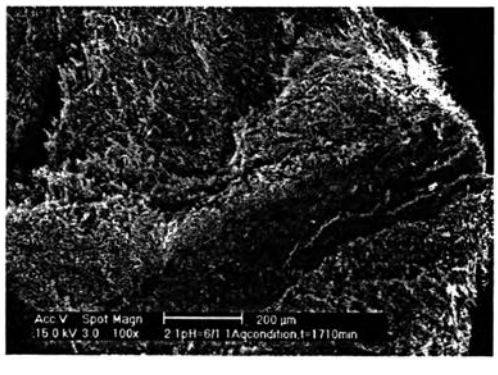
Figure 4.7 SEM pictures of the precipitate during transformation from 2:1 to 1:1 Ca^{2+}/HEDP molar ratio

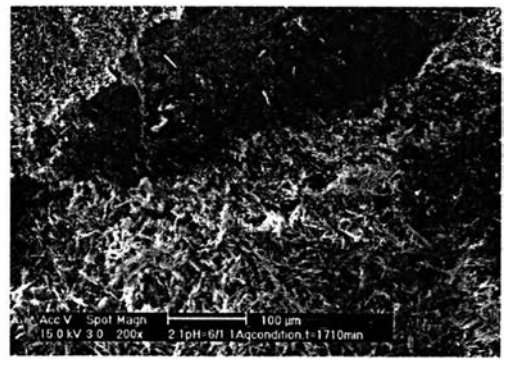


200x **750 minutes** 550x



100x **1,290 minutes** 550x





100x **1,710 minutes** 200x

Figure 4.7 - continued

The fact that transformation of spindle particle (1:1 precipitate) to spherical particle (2:1 precipitate) was much faster than transformation of spherical particle to spindle particle can be explained by 2 steps of

transformation reaction. The first step is dissolution of precipitate and the second step is the re-precipitation as described below :

		Dissolution		**Re - Precipitation**	
	Ca^{2+}/HEDP solid	➡	Ca^{2+}/HEDP liquid	➡	Ca^{2+}/HEDP solid
Case 1	1:1 solid	$\xrightarrow{k_1}$	1:1 liquid	$\xrightarrow{k_2}$	2:1 solid
Case 2	2:1 solid	$\xrightarrow{k_3}$	2:1 liquid	$\xrightarrow{k_4}$	1:1 solid

In Case 1, the 1:1 Ca^{2+}/HEDP precipitate is rapidly transformed to the 2:1 Ca^{2+}/HEDP precipitate due to the high solubility value (K_{sp}=3.02E-08 $(mol/l)^2$) of the 1:1 precipitate. Thus, it is easily dissolved and can immediately form the 2:1 precipitate.

Analogously, in Case 2, the 2:1 precipitate has a low solubility value (K_{sp}=8.12E-12 $(mol/l)^3$), then it is harder to be dissolved and slowly transformed to the 1:1 precipitate. This reason can also be further supported by the kinetics theory. From the results described in the next section, it can be used to explain that the rate of dissolution (k_1=1.40E-04 min^{-1}) and the rate of precipitation (k_2) of Case 1 are much higher than the rate of dissolution (k_3=2.01E-05 min^{-1}) and the rate of precipitation (k_4) of Case 2. That means the overall rate of reaction ($K_1=f(k_1, k_2)$) in Case 1 is higher than the overall rate of transformation ($K_2=f(k_3, k_4)$) in Case 2. The rate of dissolution (k) will be clearly discussed in the next section. Hence, the 1:1 Ca^{2+}/HEDP precipitate rapidly transformed to the 2:1 Ca^{2+}/HEDP precipitate rather than the 2:1 Ca^{2+}/HEDP precipitate transformed to the 1:1 Ca^{2+}/HEDP precipitate.

I19584914

4.2 Dissolution of Precipitates

4.2.1 Effects of Calcium and pH on the Dissolution rate of Ca^{2+}/HEDP Precipitates

The dissolution rates of both 1:1 and 2:1 Ca^{2+}/HEDP precipitates in continuous flow pattern of the differential reactor (semi-batch) were studied using dissolving fluids having different calcium concentrations as model formation water and deionized water. Two concentrations of calcium chloride in the model formation water at pH 5.5 were 1,230 and 123,000 ppm while deionized water was free from calcium and kept at pH 6.3 in order to determine the effects of calcium and pH on the precipitate dissolution rate.

Figures 4.8 and 4.9 show the effects of calcium and the pH of the dissolving fluid on the dissolution of the 1:1 and 2:1 precipitates, respectively. As can be seen from Figure 4.8, the percentage of precipitate dissolution decreases significantly with increasing calcium chloride concentration in the dissolving fluid. For a given volume of the dissolving fluid of 60 ml, the percentage of the precipitate dissolution was 70.94 and 55.70 % for the calcium chloride concentration in the model formation water of 1,230 and 123,000 ppm, respectively. For the case of deionized water, the percentage of precipitate dissolution was 41.80 % when 60 ml of deionized water was fed through the precipitate. The results reveal that an increase in the pH of the dissolving fluid also decreased the percentage of the precipitate dissolution. The effects of the solution pH on the precipitate dissolution will be discussed further in the next section. Figure 4.9 also shows the similar results for the 2:1 precipitate. For using the dissolving liquid volume of 60 ml, the percentages of precipitate dissolution were 56.60 %, 21.16 % and 9.15 % corresponding to the model formation water having 1,230 ppm $CaCl_2$, 123,000 ppm $CaCl_2$ and deionized water, respectively. For the experimental results, it can be concluded that it is much more difficult to dissolve a 2:1 Ca^{2+}/HEDP

precipitate than a 1:1 Ca^{2+}/HEDP precipitate. The effect of calcium on the precipitate dissolution can be explained by Le-Chatlier principle as shown in the chemical equilibrium equation below :

$$Ca^{2+} + HEDP^{-2} \longleftrightarrow CaHEDP\downarrow \quad (4.1)$$

$$Ca^{2+} + CaHEDP\downarrow \longleftrightarrow Ca_2HEDP\downarrow + 2H^{+} \quad (4.2)$$

For the case of the 1:1 precipitate, a decrease in calcium results in increasing the precipitate dissolution as explained by equation (4.1) which forces the reaction shifting to left hand side. For the case of the 2:1 precipitate, analogously, an increase in calcium concentration will force the reaction shift to the left hand side. This means that the dissolution of the precipitate then decreases with increasing the calcium concentration in the dissolving solution. The dissolution rate of the 2:1 precipitate is simply slower than the dissolution rate of the 1:1 precipitate since the 2:1 precipitate has to transform to the 1:1 precipitate first.

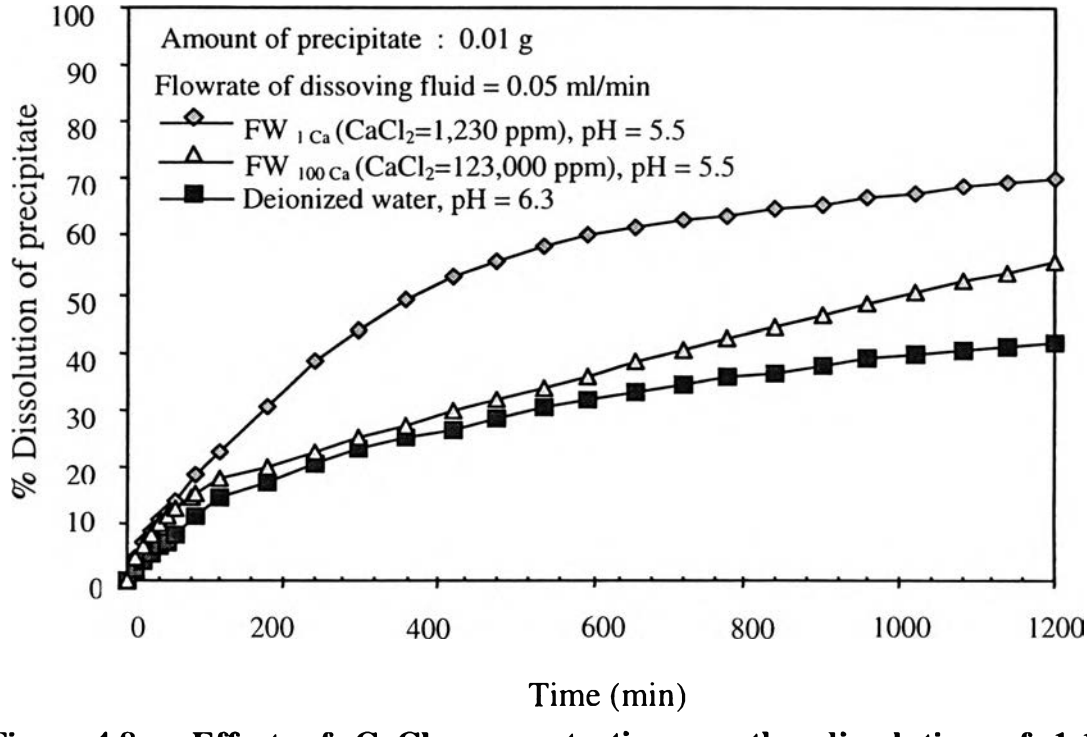


Figure 4.8 Effect of $CaCl_2$ concentration on the dissolution of 1:1 Ca^{2+}/HEDP precipitate

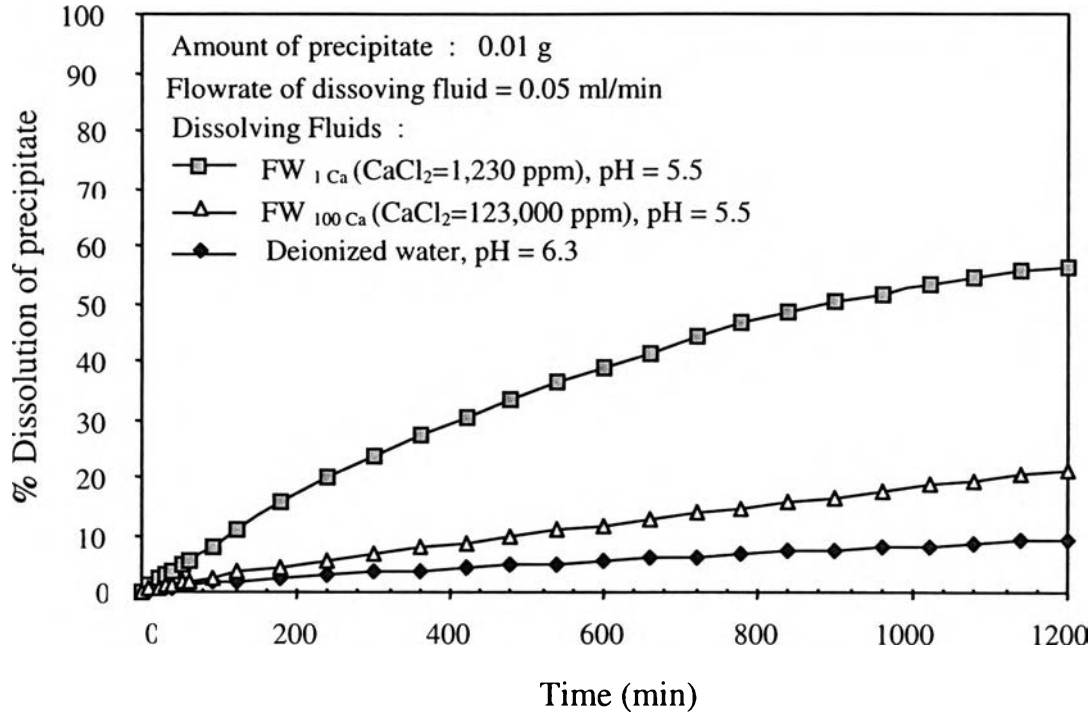


Figure 4.9 Effect of $CaCl_2$ concentration on the dissolution of 2:1 Ca^{2+}/HEDP precipitate

As can be seen from Figures 4.8 and 4.9, the dissolution rates of both 1:1 and 2:1 precipitates decreased with increasing both calcium concentration and pH. The effect of calcium on the dissolution rate of precipitates can be desorbed by their solubility product (K_{sp}) as shown in equations 4.3 and 4.4.

For 1:1 precipitate :

$$K_{sp,1} = \frac{[Ca^{2+}][HEDP^{2-}]}{[CaHEDP]} \qquad (4.3)$$

For 2:1 precipitate :

$$K_{sp,2} = \frac{[Ca^{2+}]^2[HEDP^{3-}]}{[Ca_2HEDP]} \qquad (4.4)$$

When the calcium concentration in the dissolving fluid increases, the dissolution rates of both 1:1 and 2:1 precipitates decrease as seen from equations 4.3 and 4.4.

4.2.2 Determination of Dissolution Rate Constant

Figure 4.10 shows the plot to determine the values of the dissolution rate constant of both 1:1 and 2:1 precipitates with different dissolving fluids. Table 4.1 gives the calculated values of the dissolution rate constant. As can be seen from Table 4.1, the dissolution rate of the precipitate depends on the precipitate type, calcium concentration and the solution pH. The effect of pH is much greater than the effect of calcium on the dissolution rate.

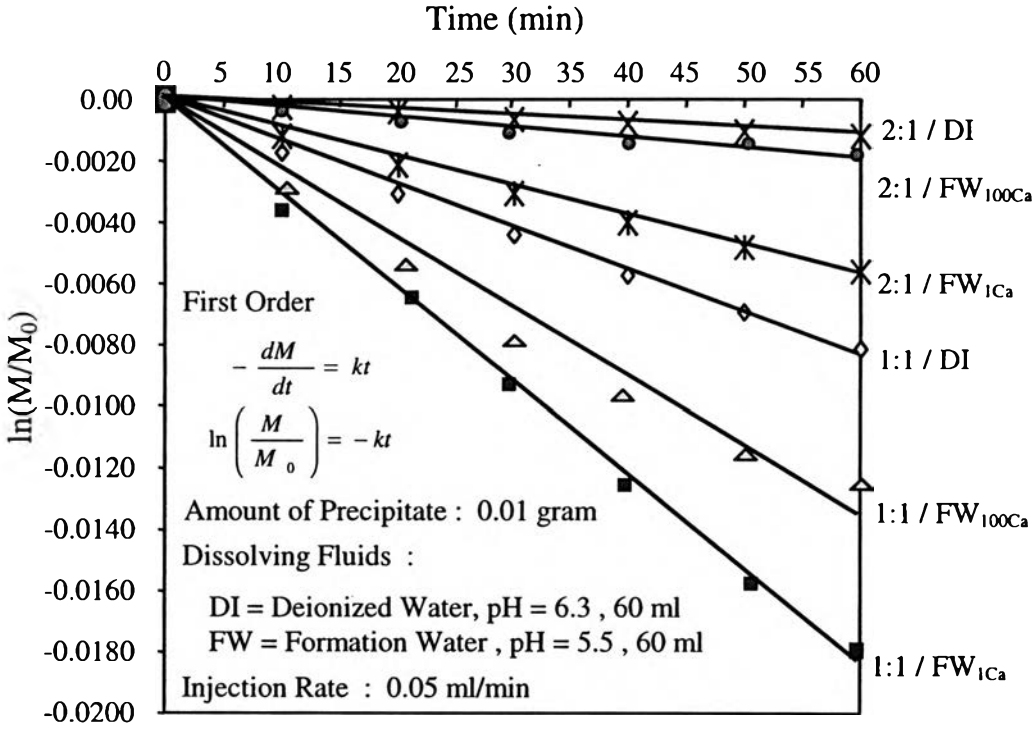


Figure 4.10 Kinetics study of initial dissolution rate of both 1:1 and 2:1 Ca^{2+}/HEDP precipitates in differential reactor using different calcium concentrations and solution pHs

Table 4.1 The values of the dissolution rate constant of 1:1 and 2:1 precipitates by deionized water and model formation water

Dissolving Fluid	Dissolution Rate Constant (k) min^{-1}	
	1:1 precipitate	2:1 precipitate
1,230 ppm $CaCl_2$ formation water ($FW_{1\ Ca}$)	2.60E-04	9.67E-05
123,000 ppm $CaCl_2$ formation water ($FW_{100\ Ca}$)	2.34E-04	3.42E-05
Deionized Water	1.40E-04	2.01E-05

4.3 Precipitate Release in Micromodel

As be described ealier, two different Ca^{2+}/HEDP precipitates could be formed by controlling the solution pH. This section was to attempt visual observations of the formation, displacement and subsequent release of both 1:1 and 2:1 Ca^{2+}/HEDP precipitates in a pseudo porous medium using model formation water and deionized water. The resulting data can be used to predict the squeeze lifetime of HEDP inhibitor which initially forms both 1:1 and 2:1 Ca^{2+}/HEDP precipitates.

i Release of 1:1 Ca^{2+}/HEDP precipitate

A 1:1 Ca^{2+}/HEDP precipitate was placed in the micromodel. The micromodel was then eluted with the model formation water containing of 1,230 ppm and 123,000 ppm of $CaCl_2$ at pH=5.5 and deionized water at pH=6.3. A flowrate of dissolving fluid was kept constant at 0.05 ml/min. The elution curves and micromodel images were then compared to determine the

release of phosphonate with three different dissolving fluids.

The 1:1 Ca^{2+}/HEDP precipitate formed in the micromodel appeared as fibrous-like spindles similar to those synthesized. The precipitates formed were formed compacting at pore throats. After injecting any dissolving fluid into the micromodel, saturated Ca^{2+}/HEDP solution in contact with the precipitate is firstly swept from the micromodel, resulting in the high HEDP concentration seen in the elution curve and gradually decreases as shown in Figures 4.11 and 4.12. A similar trend was obtained when $CaCl_2$ concentration in the elution fluid was increased to 123,000 ppm (see Figures 4.13 and 4.14) For having the minimum effective concentration of HEDP, the release lifetime could increase approximately 4 times when the calcium chloride concentration in the model formation water increased from 1,230 ppm to 123,000 ppm. Figures 4.15 and 4.16 show the elution curve and the progressive dissolution of the 1:1 precipitate when deionized water was employed as elution fluid. The effect of the solution pH can be simply elucidated by comparing the elution curves shown in Figures 4.11 and 4.15. A conclusion can be drawn that an increase in the pH of the formation water will result in increasing the release lifetime of HEDP.

Figures 4.12, 4.14 and 4.16 illustrate the photographs of the precipitates to be dissolved gradually. The precipitate was rapidly dissolved as shown the disappearance of the fibrous solids situating in pores and pore throats. Then, the remaining precipitate consisted of densely packed fibers only confined at the pore throats causing extremely slow release of HEDP from the micromodel which corresponded to a long tail of the elution curve.

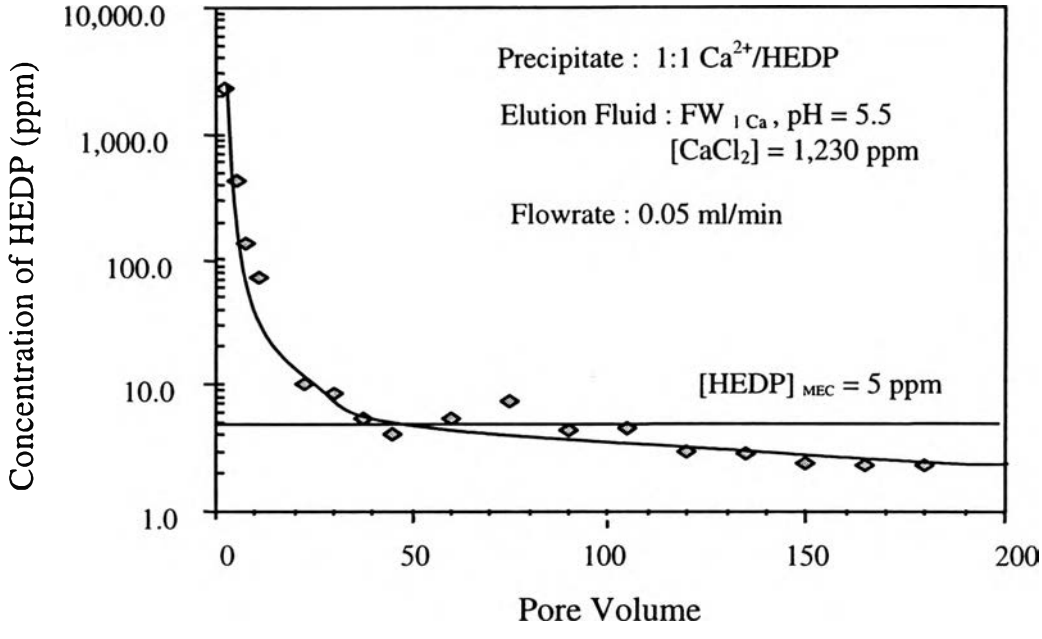
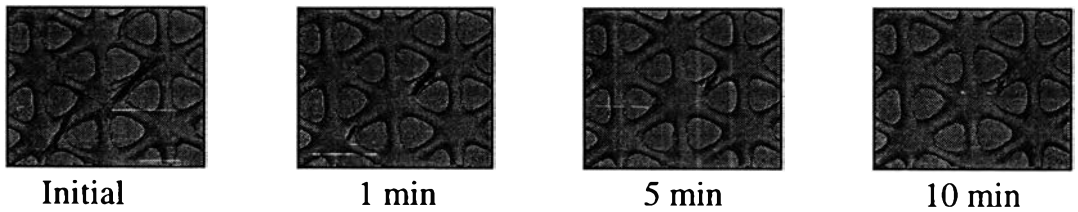


Figure 4.11 Elution curve of 1:1 Ca^{2+}/HEDP precipitate by 1,230 ppm $CaCl_2$ model formation water at pH=5.5



Initial	1 min	5 min	10 min
PV = 0	PV = 0.25	PV = 1.25	PV = 2.50

Figure 4.12 Sequential release of 1:1 Ca^{2+}/HEDP precipitate from micromodel by 1,230 ppm $CaCl_2$ model formation water at pH=5.5

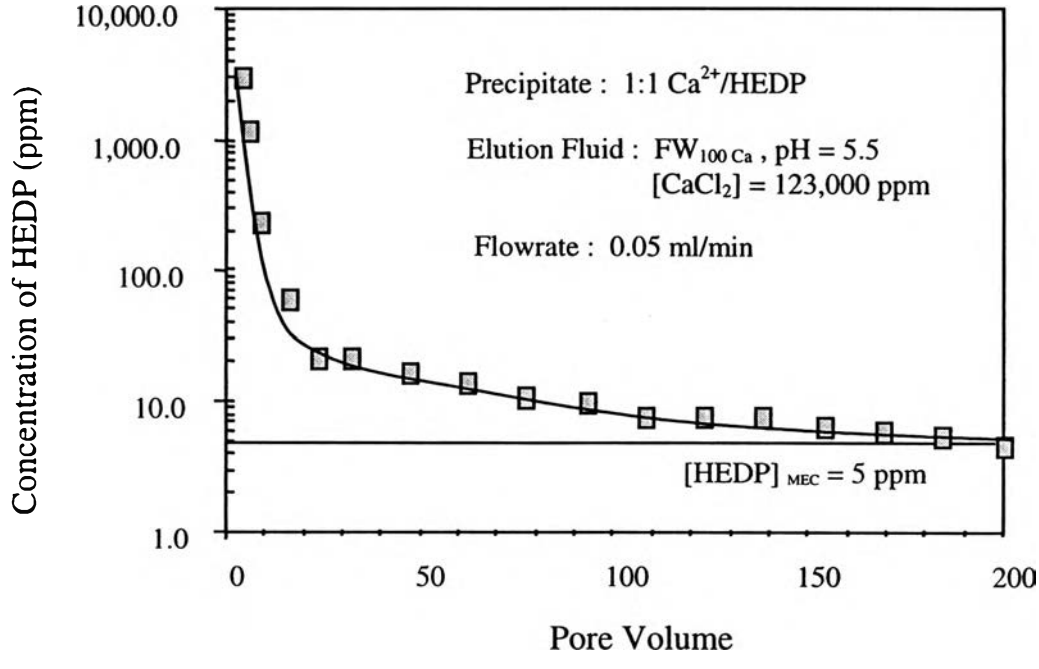


Figure 4.13 Elution curve of 1:1 Ca^{2+}/HEDP precipitate by 123,000 ppm $CaCl_2$ model formation water at pH=5.5

Initial	3 min	10 min	360 min
PV = 0	PV = 0.75	PV = 2.50	PV = 90

Figure 4.14 Sequential release of 1:1 Ca^{2+}/HEDP precipitate from micromodel by 123,000 ppm $CaCl_2$ model formation water at pH=5.5

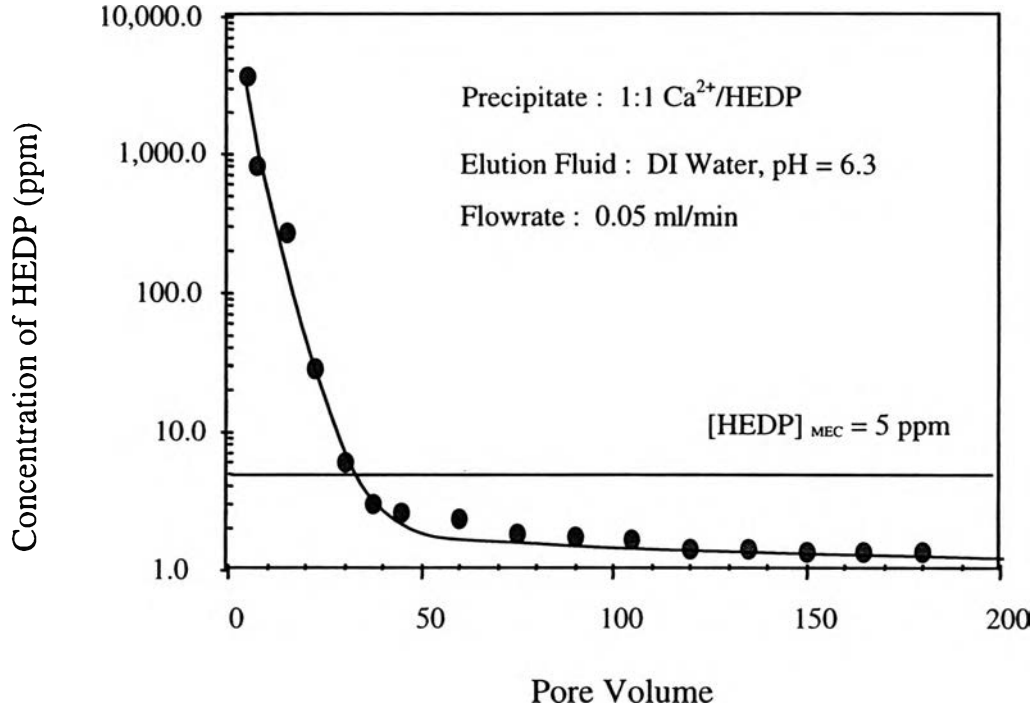


Figure 4.15 Elution curve of 1:1 Ca^{2+}/HEDP precipitate by deionized water at pH=6.3

Initial	3 min	5 min	10 min
PV = 0	PV = 0.75	PV = 1.25	PV = 2.50

Figure 4.16 Sequential release of 1:1 Ca^{2+}/HEDP precipitate from micromodel by deionized water at pH=6.3

ii Release of 2:1 Ca^{2+}/HEDP precipitate

The second precipitate that was examined in the micromodel was the 2:1 Ca^{2+}/HEDP precipitate, which had been synthesized as described in the previous section. The precipitate was powdery and spherical and it could be dissolved very slowly as desorbed earlier. The procedure for precipitate placement and elution was identical to that in the 1:1 Ca^{2+}/HEDP precipitate. The precipitate in the micromodel was formed in powedery and spherical particles situated in both pore bodies and pore throats. The saturated solution initially in contact with the precipitate was swept from the micromodel. The high HEDP concentration initially showed in the elution curve (see Figures 4.17, 4.19, and 4.21). The release of phosphonate from the 2:1 precipitate was dominated by a very slow dissolution rate as compared to the 1:1 precipitate. Figures 4.18,4.20, and 4.22 show how slow the phosphonate releases from the porous media by 1,230 ppm and 123,000 ppm $CaCl_2$ in model formation water at pH=5.5 and deionized water at pH=6.3, respectively.

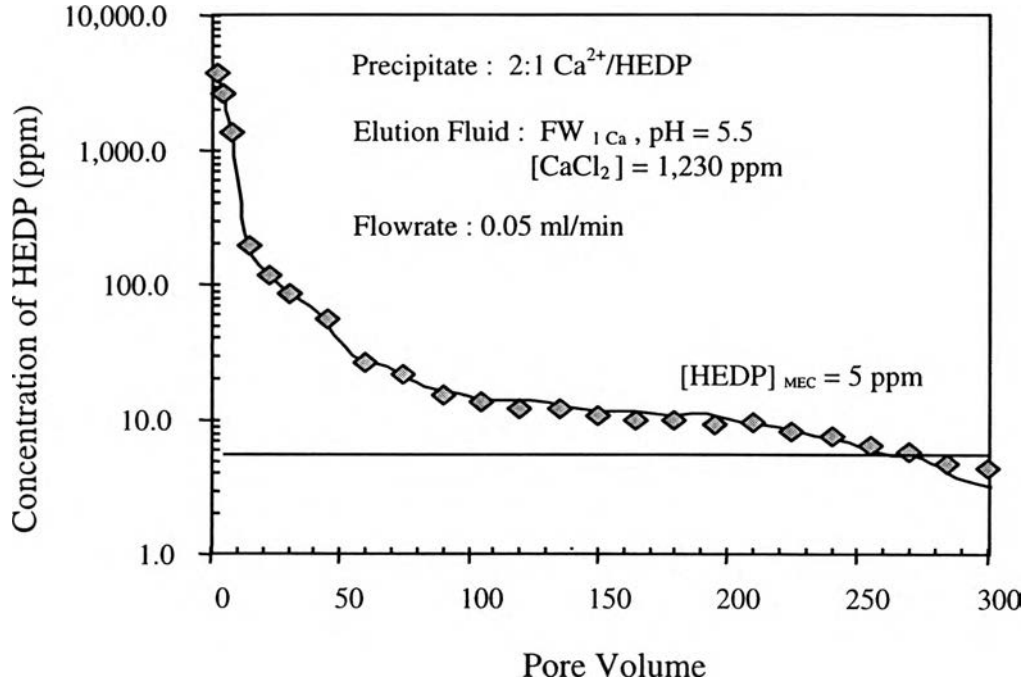
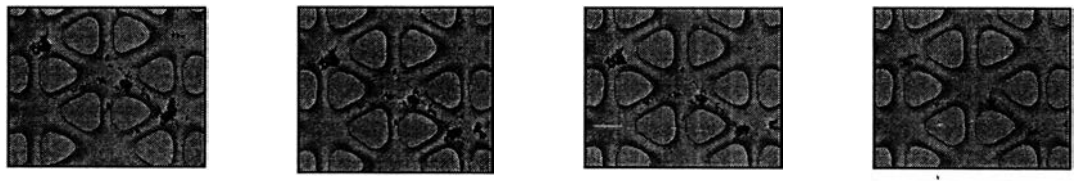


Figure 4.17 Elution curve of 2:1 Ca^{2+}/HEDP precipitate by 1,230 ppm $CaCl_2$ model formation water at pH=5.5



Initial	60 min	90 min	120 min
PV = 0	PV = 15	PV = 22.5	PV = 30

Figure 4.18 Sequential release of 2:1 Ca^{2+}/HEDP precipitate from micromodel by 1,230 ppm $CaCl_2$ model formation water at pH=5.5

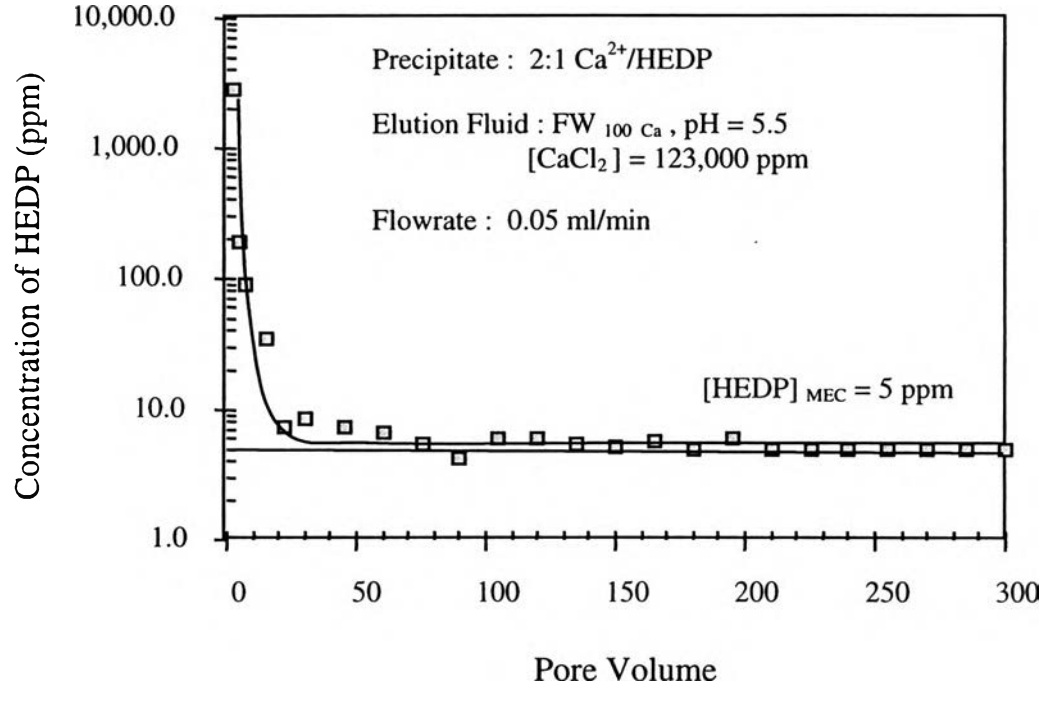


Figure 4.19 Elution curve of 2:1 Ca^{2+}/HEDP precipitate by 123,000 ppm $CaCl_2$ model formation water at pH=5.5

Initial	60 min	180 min	360 min
PV = 0	PV = 15	PV = 45	PV = 90

Figure 4.20 Sequential release of 2:1 Ca^{2+}/HEDP precipitate from micromodel by 123,000 ppm $CaCl_2$ model formation water at pH=5.5

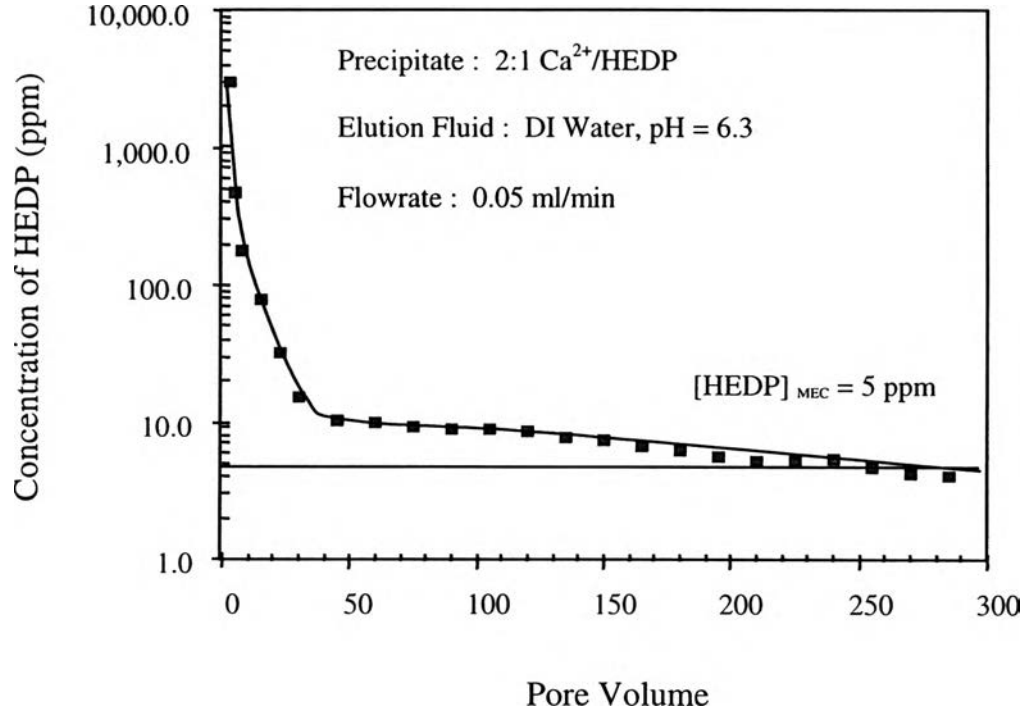
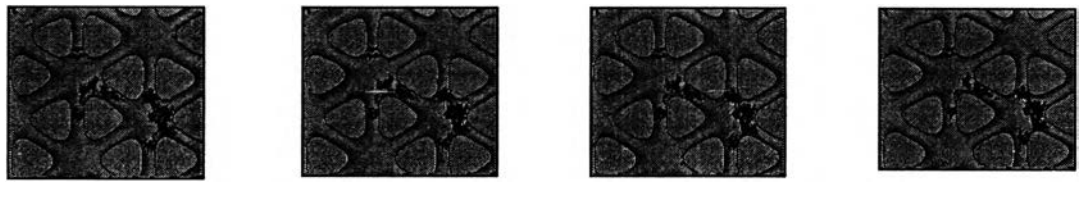


Figure 4.21 Elution curve of 2:1 Ca^{2+}/HEDP precipitate by deionized water at pH=6.3



Initial	60 min	90 min	180 min
PV = 0	PV = 15	PV = 22.5	PV = 45

Figure 4.22 Sequential release of 2:1 Ca^{2+}/HEDP precipitate from micromodel by deionized water at pH=6.3

4.3.1 Effect of Precipitate Molar Ratio on the Release Process

By comparing the release characteristics of both 1:1 and 2:1 Ca^{2+}/HEDP precipitates from the micromodel, the different precipitate properties were favorable in enhancing the treatment lifetimes. For the 1:1 Ca^{2+}/HEDP precipitate, the morphology was such that strong pore throat plugs could form to slow the release of phosphonate and enhance the squeeze lifetime although the dissolution rate was relatively high. For the 2:1 Ca^{2+}/HEDP precipitate, the dissolution rates were sufficiently slow so that the elution curves had long tails, which is extremely beneficial for improving scale treatments.

From all of the elution curves obtained from this study, although changing the elution fluids from no calcium amount in deionized water to there was some calcium in the model formation water, both 1:1 and 2:1 Ca^{2+}/HEDP precipitates still performed the similar manner in their own releasing processes.

4.3.2 Effect of Calcium on the Elution of Ca^{2+}/HEDP Precipitates

The effect of calcium played an important role in enhancing the treatment lifetime of HEDP phosphonate. The elution results from the micromodel experiment also showed the agreement data of the HEDP release of both 1:1 and 2:1 Ca^{2+}/HEDP precipitates with 1,230 ppm and 123,000 ppm of $CaCl_2$ in the model formation water. The higher the calcium concentration in the model formation water was applied, the more enhancement squeeze lifetime was obtained.

As can be seen from Figure 4.23, for the release of HEDP from the 1:1 Ca^{2+}/HEDP precipitate, the longer treatment lifetime can be achieved by introducing excess amount of calcium cation in the model formation water.

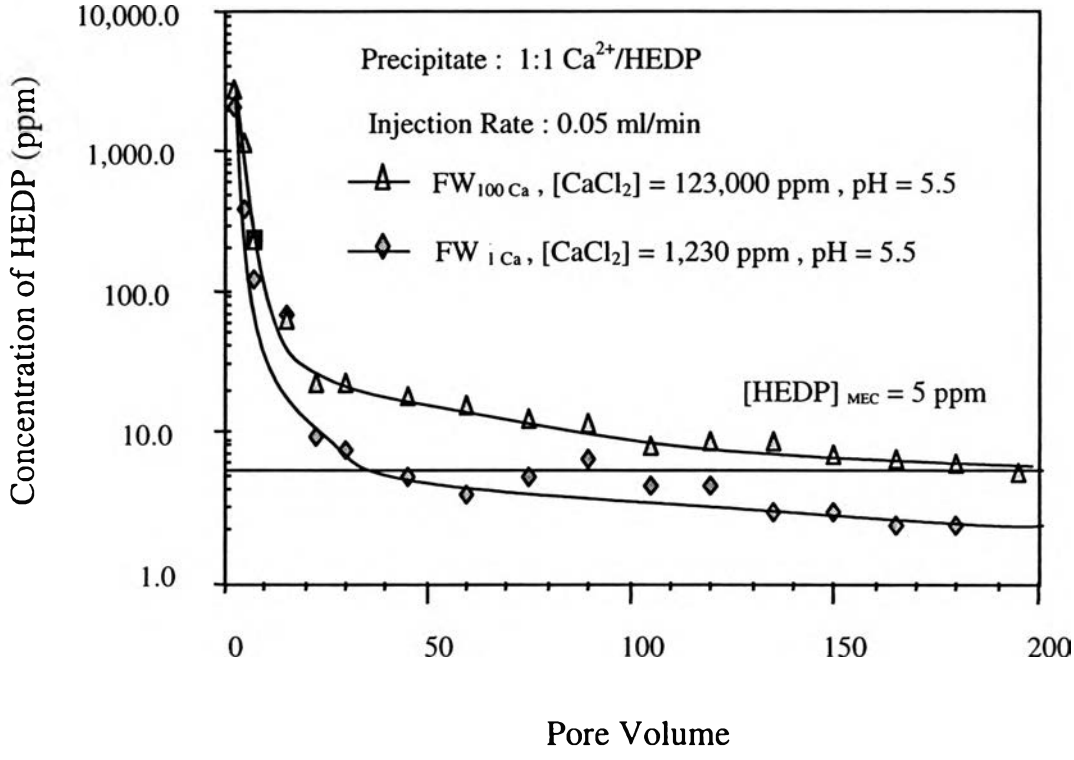


Figure 4.23 Effect of calcium on the HEDP release of the 1:1 Ca^{2+}/HEDP precipitate in micromodel

In case of the 2:1 Ca^{2+}/HEDP precipitate as shown in Figure 4.24, the results could not see much difference in the elution curve for enhancing the phosphonate lifetime but one can notice that for eluting the precipitate with 123,000 ppm of $CaCl_2$ in the model formation water, the release of HEDP above the minimum effective concentration can be prolonged when compared to the use of 1,230 ppm of $CaCl_2$ in the model formation water. It can be concluded that the higher calcium concentration still give the longer treatment lifetime for the 2:1 precipitate.

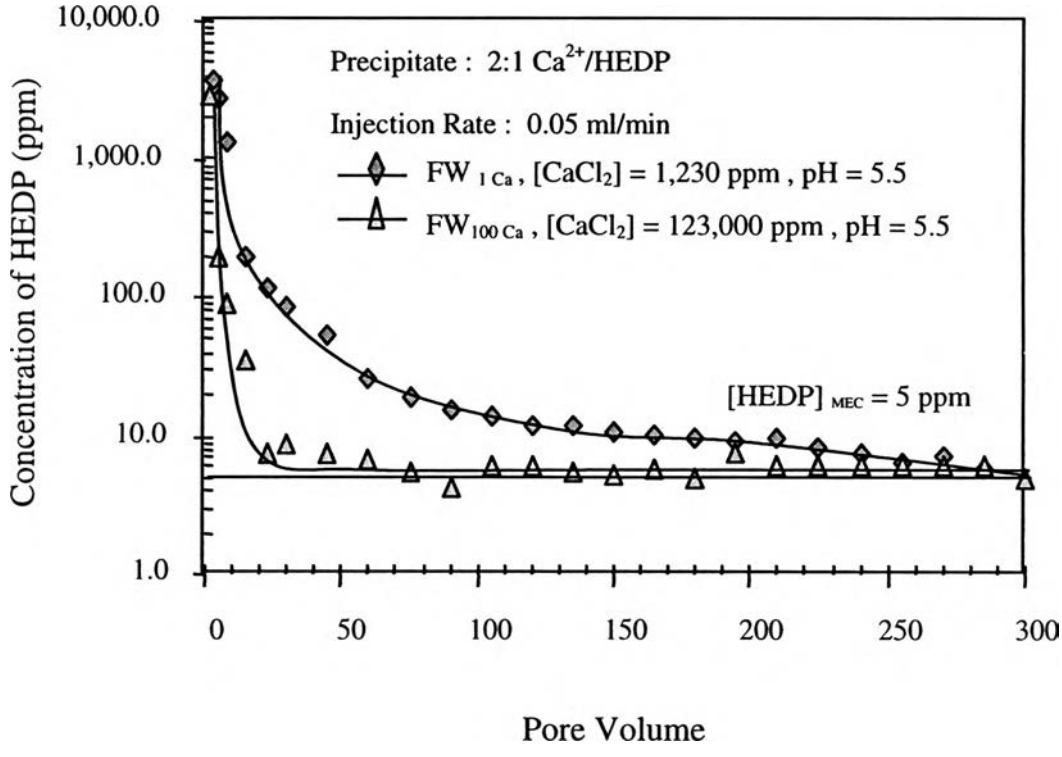


Figure 4.24 Effect of calcium on the HEDP release of the 2:1 Ca^{2+}/HEDP precipitate in micromodel

4.3.3 Effect of Calcium and pH on the Elution of Ca^{2+}/HEDP Precipitates

Generally, pH is always one of the most important effects on the dissolution process. Brine water injected into oil fields normally has a pH around 6. Hence, in this study, deionized water without calcium was adjusted to have a pH of 6.3 which was then used as an elution fluid. As be shown in Figures 4.25 and 4.26, deionized water is the worst elution fluid to enhance the longer lifetime of phosphonate for both precipitates. There are two combining reasons to be considered to explain these results. First, a higher pH causes more difficulty to dissolve the precipitate out from the micromodel and hence it results in the lower release of phosphonate from the micromodel. The second effect of calcium cation is one of the most vital parameters in this

elution as well. From the results, the prominent effect should come from the amount of calcium rather than the pH effect because the pH of both deionized water and formation water is not a big difference while the concentration of calcium in these elution fluids is clearly seen in high distinction. As previous explanation, the excess calcium cation in elution fluids could dissolve both 1:1 and 2:1 Ca^{2+}/HEDP precipitates slower than the less calcium cation amount. This is the reason why the model formation water containing 123,000 ppm. $CaCl_2$ is the best elution fluid, to give the longest tail of elution curve.

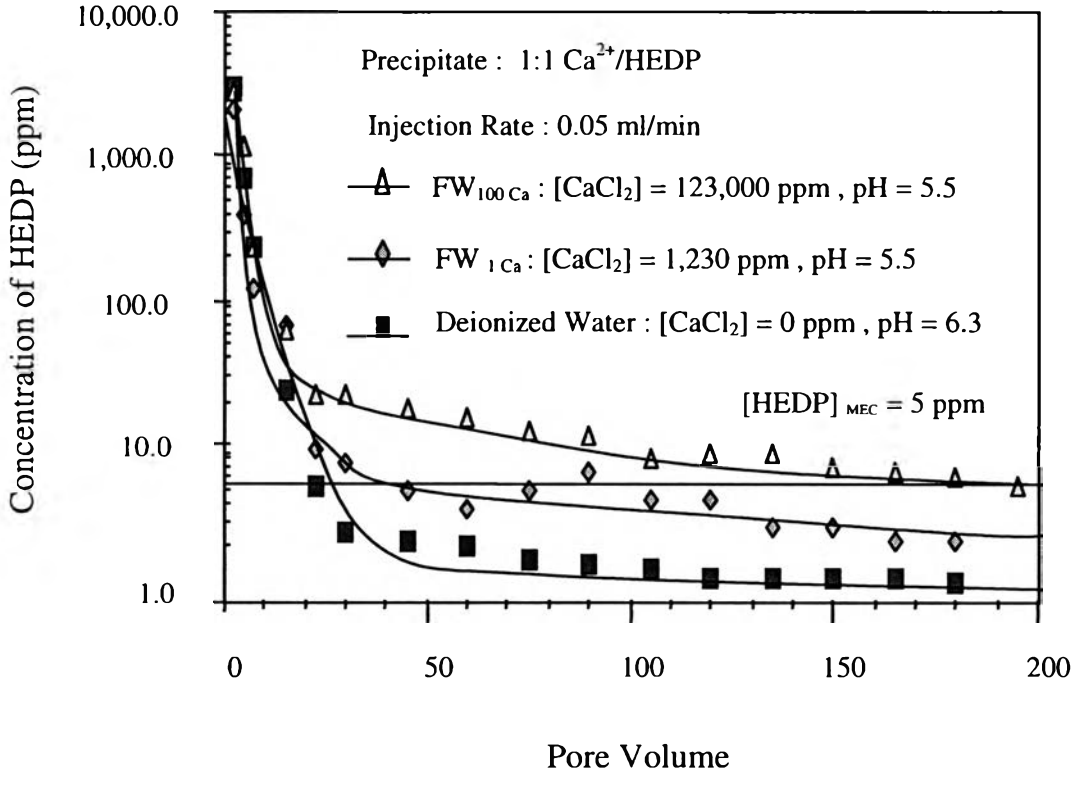


Figure 4.25 Effect of calcium in elution fluids on the 1:1 Ca^{2+}/HEDP precipitate in micromodel

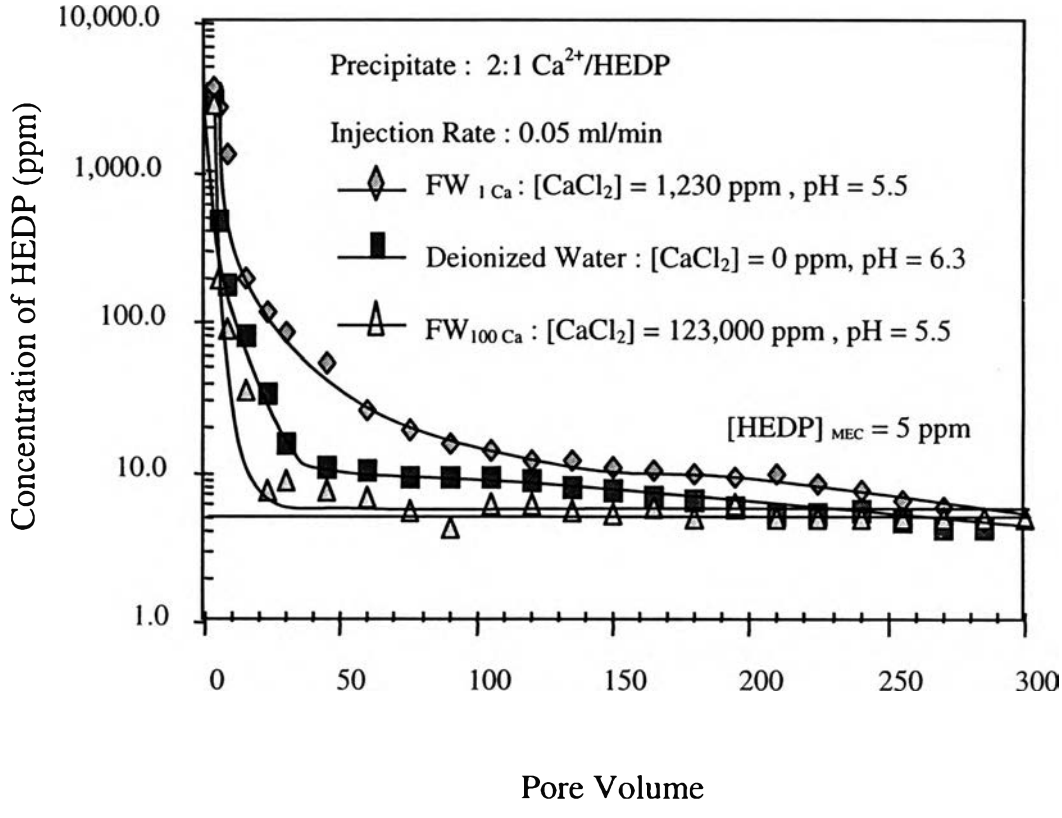


Figure 4.26 Effect of calcium in elution fluids on the 2:1 Ca^{2+}/HEDP precipitate in micromodel