

CHAPTER IV

RESULTS & DISCUSSION

There were two main parts of experiments which include batch synthesis and characterization experiments and performance of precipitates in porous media. The experimental data are given in Appendix C. These experimental results are described and discussed as below :

4.1 Batch Synthesis and Characterization

4.1.1 Morphologies of Ca-ATMP Precipitates

This section of results showed the properties of three different calcium-ATMP precipitates which formed with varying the extreme conditions. From the results shown in Table 4.1 , the precipitates were synthesized by varying the precipitating molar ratio and pH in solution. The molar product was 0.08 M^2 (0.5 M CaCl_2 and 5 % wt ATMP). The resulting precipitates were clarified the properties as below.

At a pH of 1.5 , calcium/ATMP molar ratio in precipitates was 1:1. One calcium cation attached to one active phosphate group in ATMP and formed the precipitate. Even though a large ratio of calcium/ATMP of 10:1 in solution was used during titration , the precipitate had still potential to form 1:1 precipitate. Hence, it showed that pH in solution during titration was a major factor in the formation of the 1:1 precipitate. The morphologies of this

Table 4.1 Summary of Batch Synthesis and Characterization Experiments

Experimental condition			Precipitation		
Molar product [Ca ²⁺][ATMP]	pH	Ca/ATMP Molar Ratio in solution	Ca/ATMP Molar Ratio in precipitate	Precipitate Morphology	Equilibrium Concentration (ppm)
0.08	1.5	1:1	1:1	Sheet	1221
0.08	1.5	10:1	1:1	Sheet	1216
0.08	4	1:1	2:1	Spherical Particles	961
0.08	4	10:1	2:1	Spherical Particles	487
0.08	4.5	1:1	2:1	Spherical Particles	818
0.08	4.5	12:1	2:1	Spherical Particles	639
0.08	6	1:1	2:1	Spherical Particles	453
0.08	6	10:1	3:1	Spherical Particles	332
0.08	7	1:1	2:1	Spherical Particles	x
0.1672	7	1:1	2:1	Spherical Particles	x
0.08	7	5:1	3:1	Spherical Particles	241
0.08	7	10:1	3:1	Spherical Particles	232
0.08	7-6.432	1:1	2.14	Sheet and Spherical	486
0.08	7-4.888	10:1	2.85	Sheet and Spherical	377
0.08	9	1:1	No Precipitate	x	x

CaCl₂ 0.5 M ATMP 5% Molar Product = 0.08 M²

CaCl₂ 0.5 M ATMP 10% Molar Product = 0.1672 M²

x **No analysis at this condition**

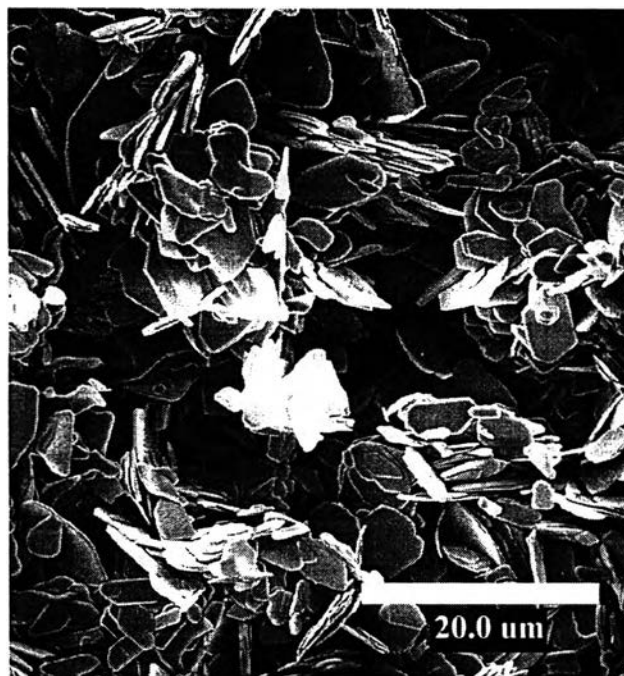


Figure 4.1 The Resulting Morphology of 1:1 Calcium/ATMP Precipitate at a pH Value of 1.5.

precipitate are sheet particles which are depicted in Figure 4.1. The limit solubility levels of these two precipitates were 1221 and 1216 ppm, respectively.

At a pH of 4.0 and 4.5 , the precipitates compounded of two calcium cations reacting with one ATMP molecule. The particles of precipitates are powdery and virtually spherical shape (see Figure 4.2 and 4.3). The morphologies of this precipitates were apparently differed from the 1:1 precipitates. The limit solubility levels of 2:1 precipitates were widely varied, for example , two equilibrium concentrations of precipitates at pH of 4.0 and 4.5 were 961 and 818 ppm , respectively.

At a pH of 6.0 , the composition of the precipitates were dependent upon the molar ratio of calcium/ATMP in solution. At a

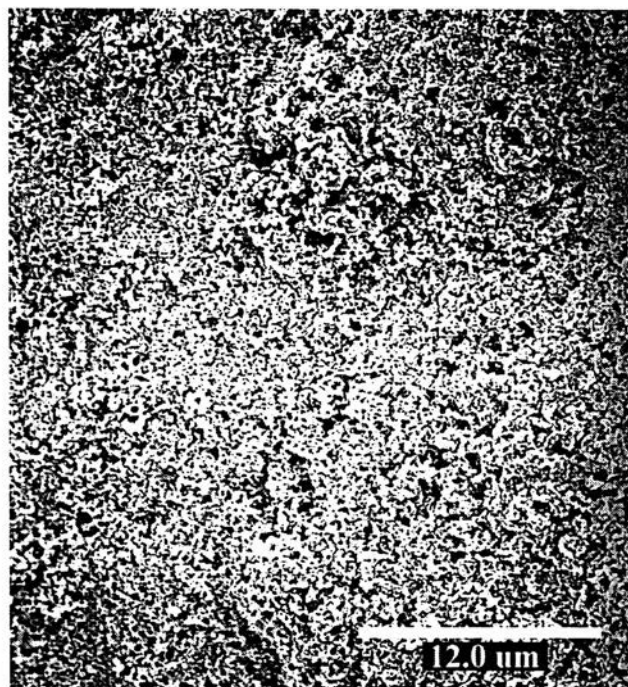


Figure 4.2 The Resulting Morphology of 2:1 Calcium/ATMP Precipitate at a pH of 4.0 and a Precipitating Molar Ratio of 1:1.

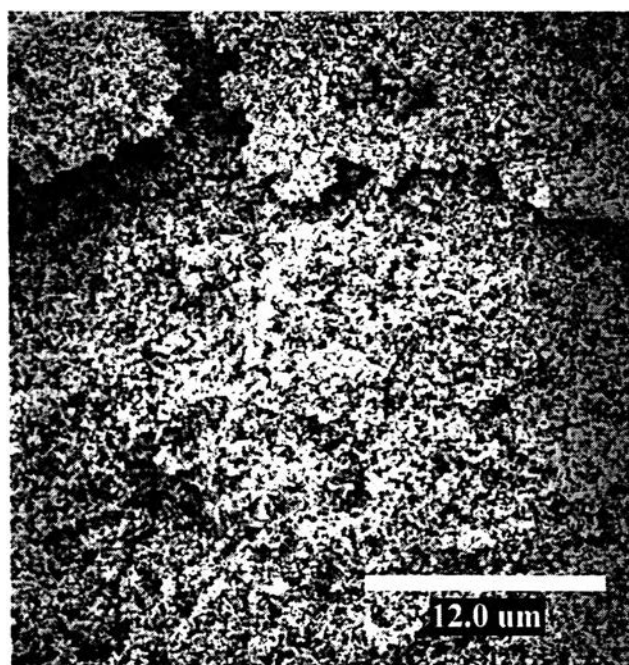


Figure 4.3 The Resulting Morphology of 2:1 Calcium/ATMP Precipitate at a pH of 4.0 and a Precipitating Molar Ratio of 10:1.

precipitating molar ratio of 1:1 and 10:1, the precipitate had a calcium/ATMP molar ratio of 2:1 and 3:1, respectively. The morphologies of 2:1 and 3:1 precipitate are powdery spherical particles (see Figure 4.4 and 4.5). The limit solubilities of 2:1 and 3:1 precipitates were 453 and 332 ppm, respectively.

At a pH of 7.0 , the calcium/ATMP molar ratios in these precipitates were 2:1 and 3:1 when a precipitating molar ratio was changed. At a precipitating molar ratio of 1:1 , 5:1 and 10:1, the precipitates had a calcium/ATMP molar ratio of 2:1 , 3:1 and 3:1 , respectively. Both precipitates also consist of powdery spherical particles (see Figure 4.6 and 4.7). However, the limit solubility level 3:1 precipitate was lower value than of 2:1 calcium/ATMP precipitate.

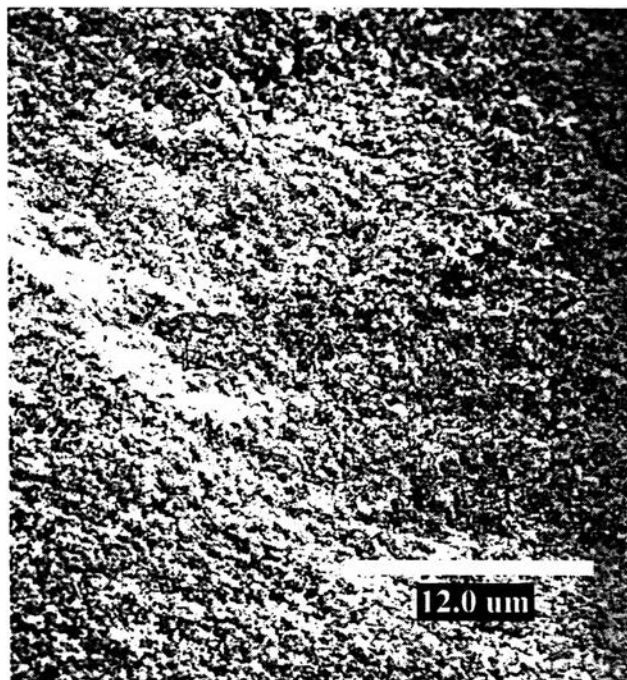


Figure 4.4 The Resulting Morphology of 2:1 Calcium/ATMP Precipitate at a pH of 6.0 and a Precipitating Molar Ratio of 1:1.

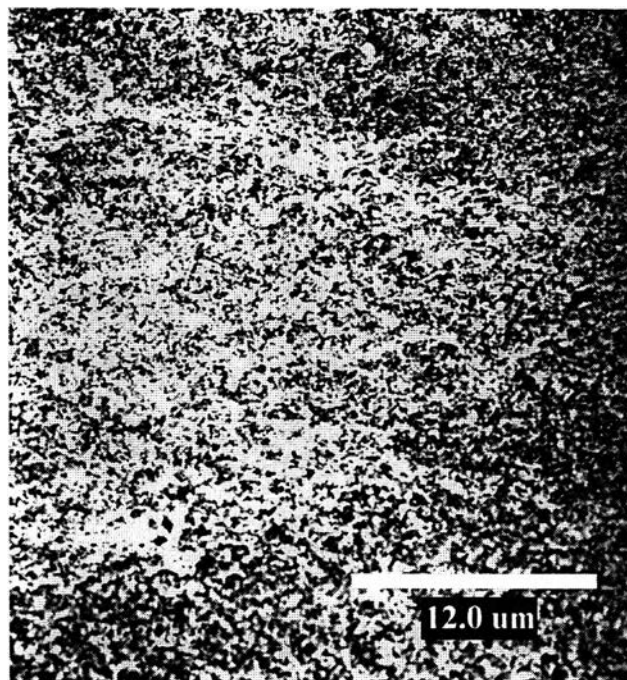


Figure 4.5 The Resulting Morphology of 3:1 Calcium/ATMP Precipitate at a pH of 6.0 and a Precipitating Molar Ratio of 10:1.

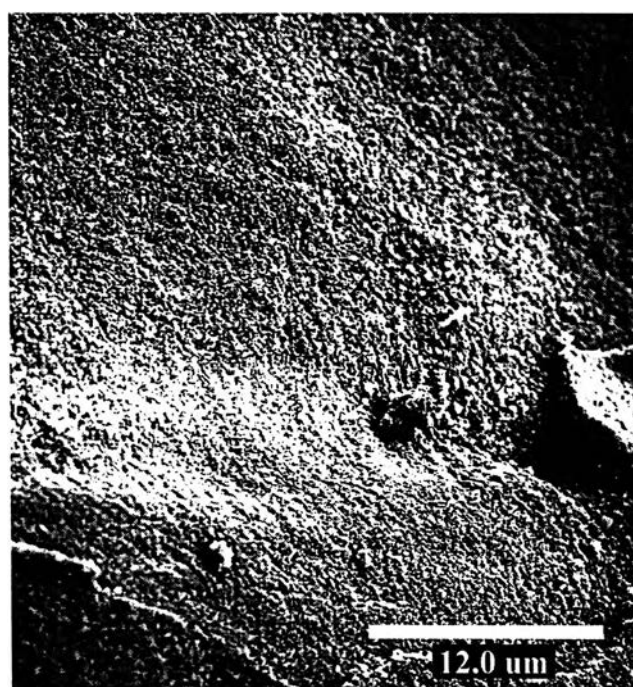


Figure 4.6 The Resulting Morphology of 3:1 Calcium/ATMP Precipitate at a pH of 7.0 and a Precipitating Molar Ratio of 5:1.

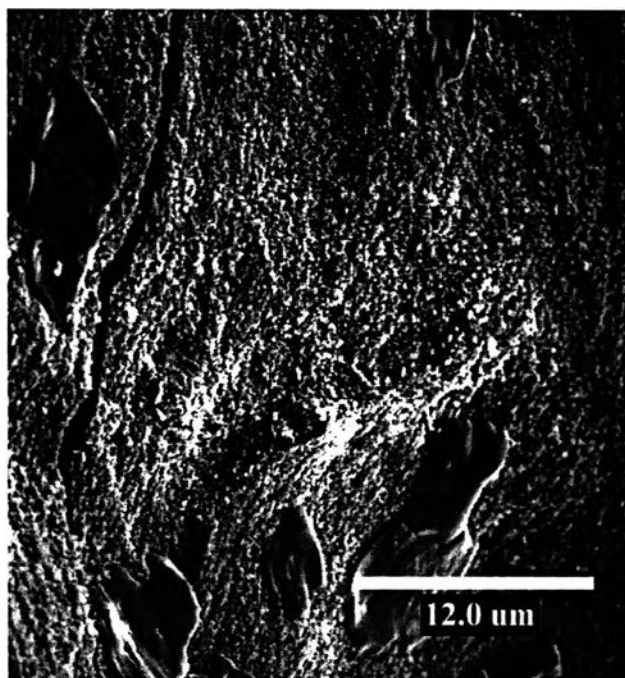


Figure 4.7 The Resulting Morphology of 3:1 Calcium/ATMP Precipitate at a pH of 7.0 and a Precipitating Molar Ratio of 10:1.

At a varying pH of 7 - 6.432 , the precipitating condition used in this formation of the precipitate was differed from the three different precipitates. Initially, the precipitate was formed by raising the reactant's pH to 7 and allowing the pH to vary after mixing. The resulting precipitate had a calcium/ATMP molar ratio of 2.14 for the 1:1 calcium/ATMP experiment. The morphology of this precipitate consists of spherical particles with random in sizes (see Figure 4.8). The equilibrium concentration of this precipitate shown in Table 4.1 is 486 ppm.

At a varying pH of 7 - 4.888 , the resulting precipitate had a calcium/ATMP molar ratio of 2.85 for the 10:1 calcium/ATMP experiment. The composition of this result is shown in Table 4.1 and the morphology is depicted in Figure 4.9. This ratio differed from the previous results in that the

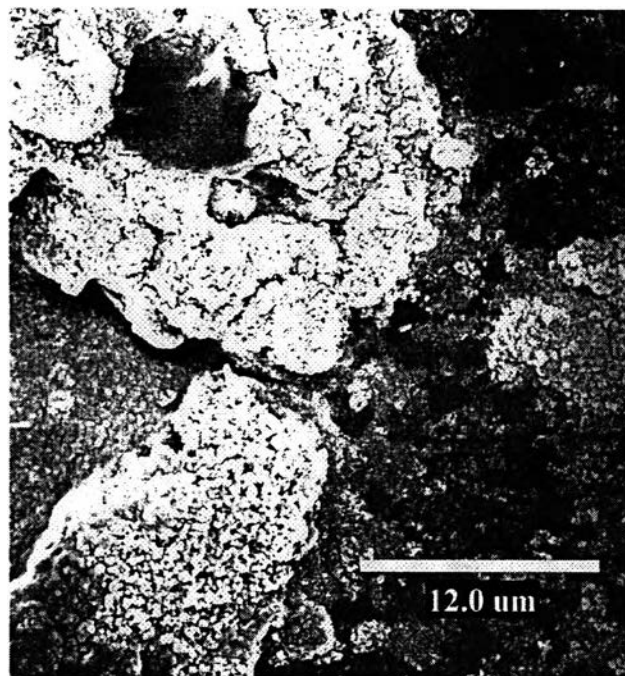


Figure 4.8 The Morphology of 2.14 Calcium/ATMP Precipitate at a pH of 7-6.432 and a Precipitating Molar Ratio of 1:1.

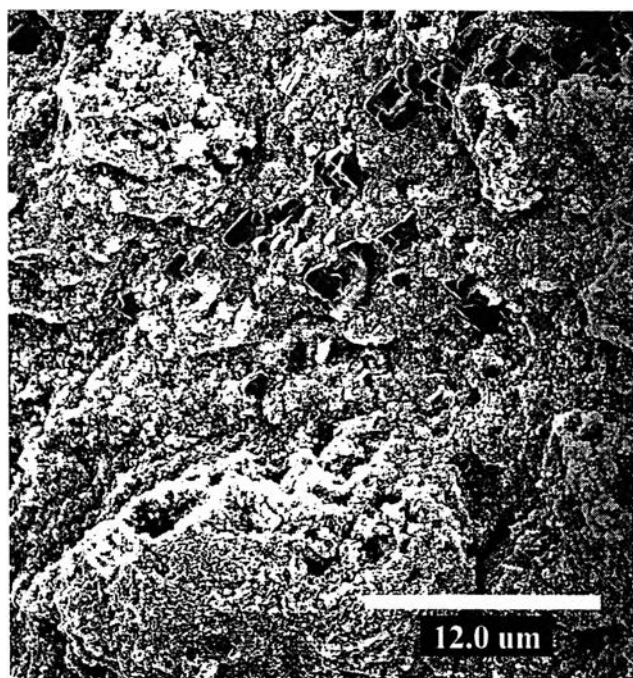
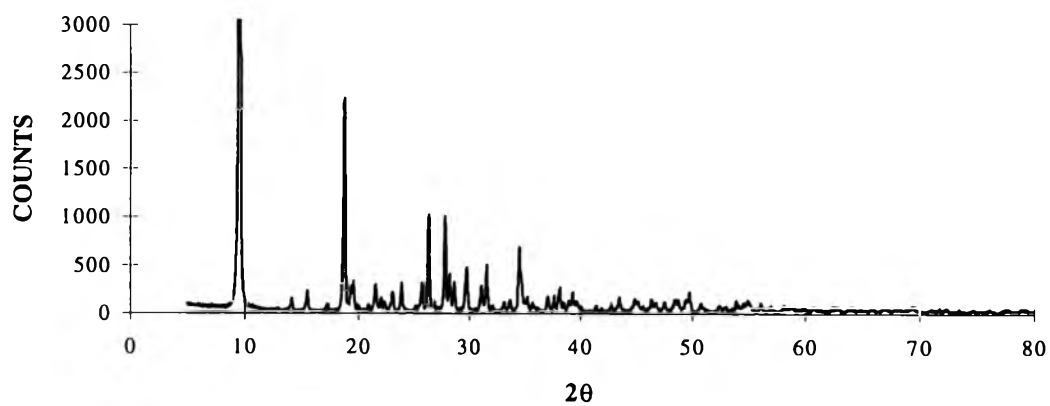


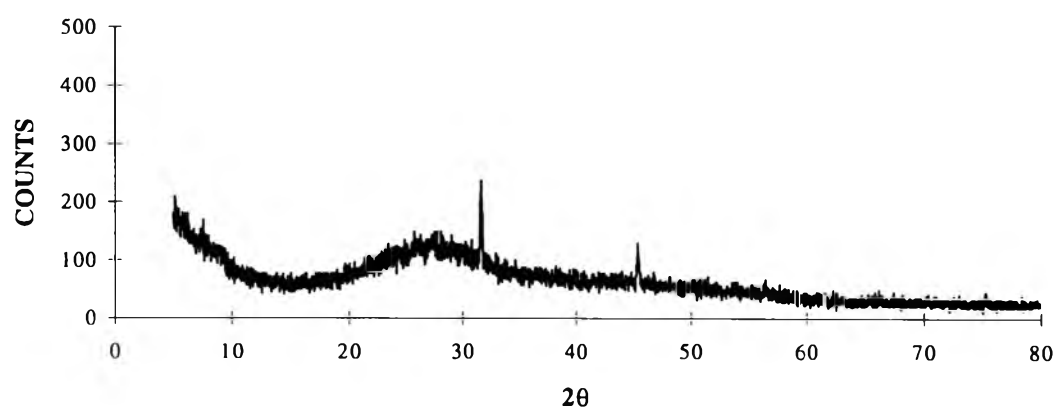
Figure 4.9 The Morphology of 2.85 Calcium/ATMP Precipitate at a pH of 7-4.888 and a Precipitating Molar Ratio of 10:1.

number of calcium cations bonding to phosphonate was not a whole number but a fraction. Also, the mixture of two precipitates can be formed by varying pH during titration. During the titration, the pH dropped and the equilibrium shifted in that the amount of hydrogens deprotonation from the ATMP molecules decreased. At the final pH value, 4.888, the maximum of four hydrogens had deprotonated and a 2:1 precipitate was possibly formed. The equilibrium concentration of this precipitate was 377 ppm.

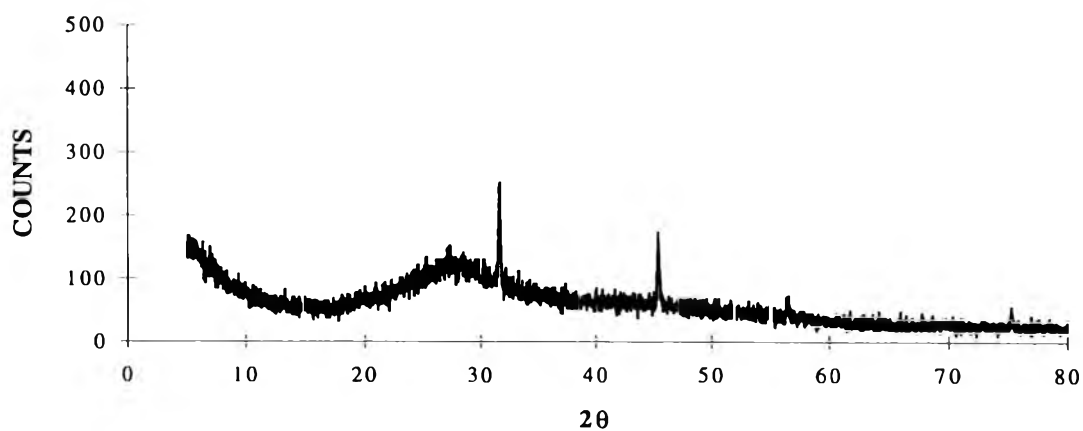
From the morphologies of three distinct precipitates, the 1:1, 2:1 and 3:1 precipitate morphologies were sheet, spherical and spherical particles, respectively. This results were supported from XRD analysis that the 1:1 precipitate had a character as the crystalline form. In contrast, both the 2:1 and 3:1 precipitates which were the amorphous forms (Figure 4.10). Figure 4.10 (a) represents the curve of the 1:1 precipitate which the peaks are apparently observed. It indicated that this precipitate was crystalline in nature. While the curves of the 2:1 and 3:1 precipitates (Figure 4.10 (b) and (c)) are looked like a flat curve and the peak are unclear which are evidently differed from the 1:1 precipitate. It indicated that the 2:1 and 3:1 precipitates were amorphous.



(a) Ca/ATMP = 1 : 1



(b) Ca/ATMP = 2:1



(c) Ca/ATMP = 3:1

Figure 4.10 XRD Patterns as a Function of Calcium/ATMP Molar Ratio.

4.1.2 Parameters Concerning with the Precipitation

The formation of precipitates in batch synthesis and characterization experiments have depended on three factors : 1) degree of supersaturation, 2) a precipitating pH, and 3) a precipitating molar ratio in solution.

4.1.2.1 The Effect of Degree of Supersaturation on the Resulting Precipitates

Two precipitates were formed at the constant pH and a precipitating molar ratio in solution but different molar product, the similarity of precipitate properties was observed. As a result of pH 7.0 (a precipitating molar ratio of 1:1 and molar product of 0.08 and 0.1672 M²), the Ca/ATMP molar ratio in precipitates of two conditions were 2:1. That means the degree of supersaturation has a little effect on the resulting precipitate's composition. From the precipitation theory, however, describes that increasing degree of supersaturation tends to increase the randomness of the nucleation and crystal growth process.

4.1.2.2 The Effect of a Precipitating pH and Ca/ATMP Molar Ratio on the Types of Precipitates

The ATMP molecules have three active phosphate groups which are available in reacting with three calcium cations. The results in Table 4.1 showed that three forms of Ca-ATMP precipitates were formed when varying a precipitating pH and Ca/ATMP molar ratio in solution.

In Figure 4.11, the types of precipitates are shown as a function of a precipitating pH and Ca/ATMP molar ratio in solution. At a precipitating molar ratio of 1:1, the stoichiometric was shifted from 1 to 2 and 2 to 3 at a pH about 4.0 and 8.0, respectively. At a precipitating molar ratio of 10:1, the stoichiometric was shifted from 1 to 2 and 2 to 3 at a pH about 3.0 and 8.0, respectively.

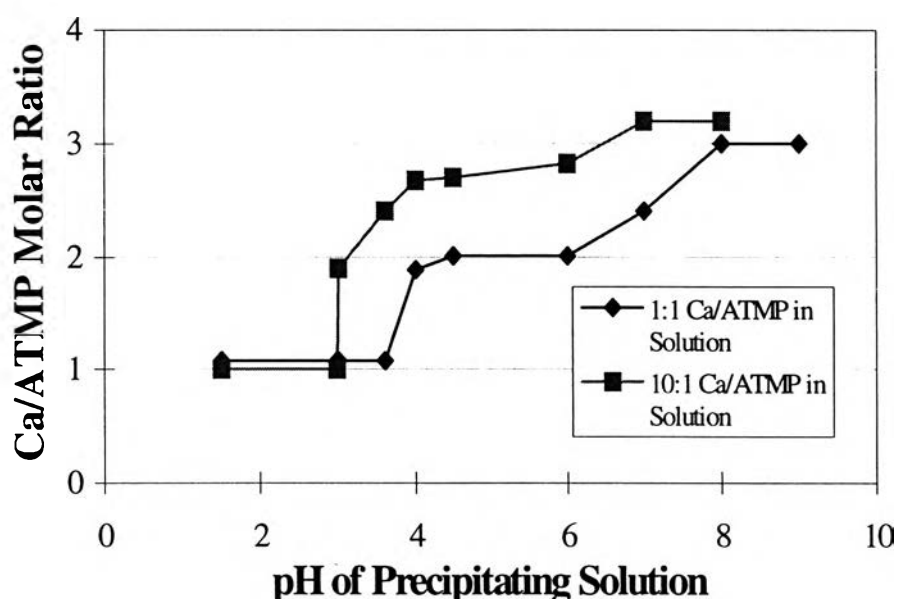


Figure 4.11 The Effect of a Precipitating pH and Molar Ratio on the Precipitates.

At low pH, the ATMP molecule has less deprotonated than at high pH because the deprotonation process is limited, leaving few sites for the calcium to attack. At higher pH, the greater deprotonation was presented and more reaction sites for the free calcium cations.

Considering the amount of calcium reacting with the ATMP molecule, the same phenomenon as an effect of pH. The excess calcium increases the probability of calcium attacking with the available

reaction sites, obtaining higher Ca/ATMP molar ratios in the resulting precipitates.

4.1.2.3 The Effect of a Precipitating pH on the Dissolution

The equilibrium concentrations of precipitates shown in Table 4.1 were depended on the effect of a precipitating pH used for synthesizing the precipitates during titration. The concentration of ATMP was monitored as a function of time until the equilibrium was approached (see Figure 4.12).

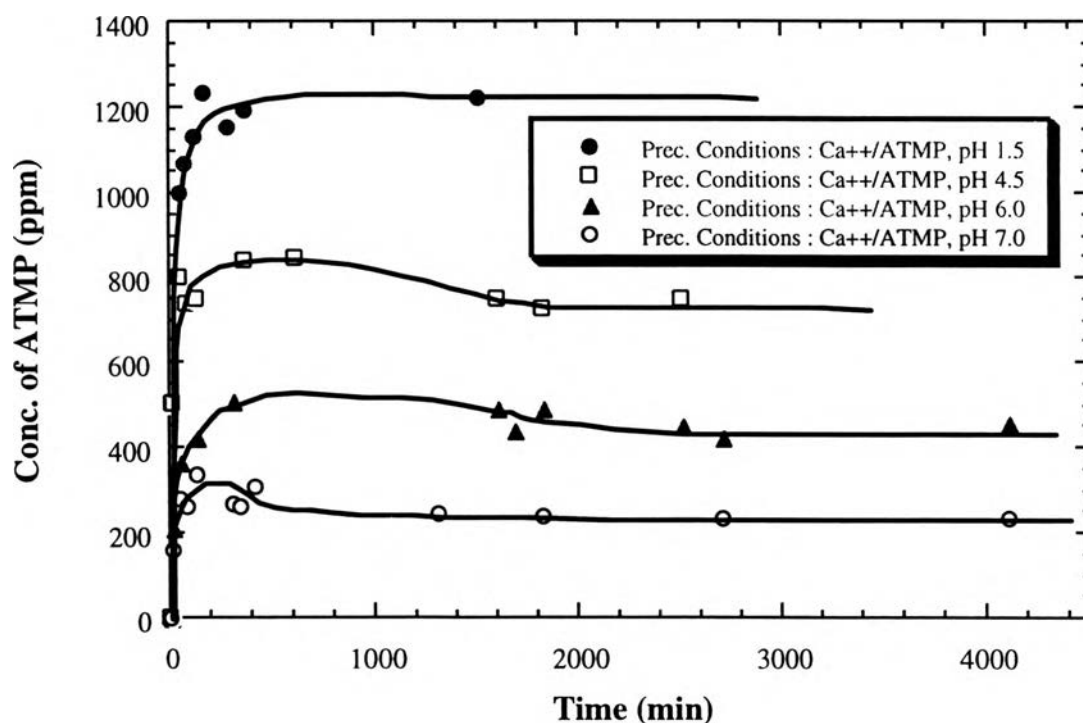


Figure 4.12 The Effect of a Precipitating pH on the Resulting Ca-ATMP Dissolution.

The precipitate formed at a precipitating pH of 1.5 gave the highest dissolution which differed from the precipitate formed at a precipitating of 7.0. Although the precipitates formed at a precipitating pH of

4.5 and 6.0 are 2:1 Ca/ATMP molar ratio precipitates (shown in Table 4.1) , but the equilibrium concentrations of each precipitates were not equal. This results supported that there were two types of 2:1 precipitates because a precipitate formed at a pH of 6.0 gave the equilibrium concentration lower than a precipitate formed at a pH of 4.5.

4.1.3 Factors Governing the Formation of Calcium - ATMP Precipitates

4.1.3.1 The Deprotonation of ATMP Molecule at the Varying pH

The deprotonation of phosphonate ATMP is changed by varying pH in the system. There are six hydrogens in ATMP which can deprotonate to each species at different pH. As shown in Figure 4.13 , the concentration of ATMP of each species is plotted as the function of solution pH. When the pH of solution is adjusted to a desired level, ATMP have deprotonated in different species as depicted in Figure 4.13.

The amount of ATMP deprotonation is clarified where the advantages offer that the chemical compositions of precipitates are predicted. The pH where the fraction of two different deprotonated species is equal defines a pKa value. Although pKa values are reported (see Figure 3.1) , but that can not be used solely to predict what type of precipitates form.

From a pKa values of ATMP, the deprotonation curves of ATMP are developed as a fraction of ATMP species. The ATMP molecule is deprotonated to the higher degree of species depended on the pH in solution.

There were five points of titrating pH which were 1.5, 4.0, 4.5, 6.0 and 7.0. in this experiment.

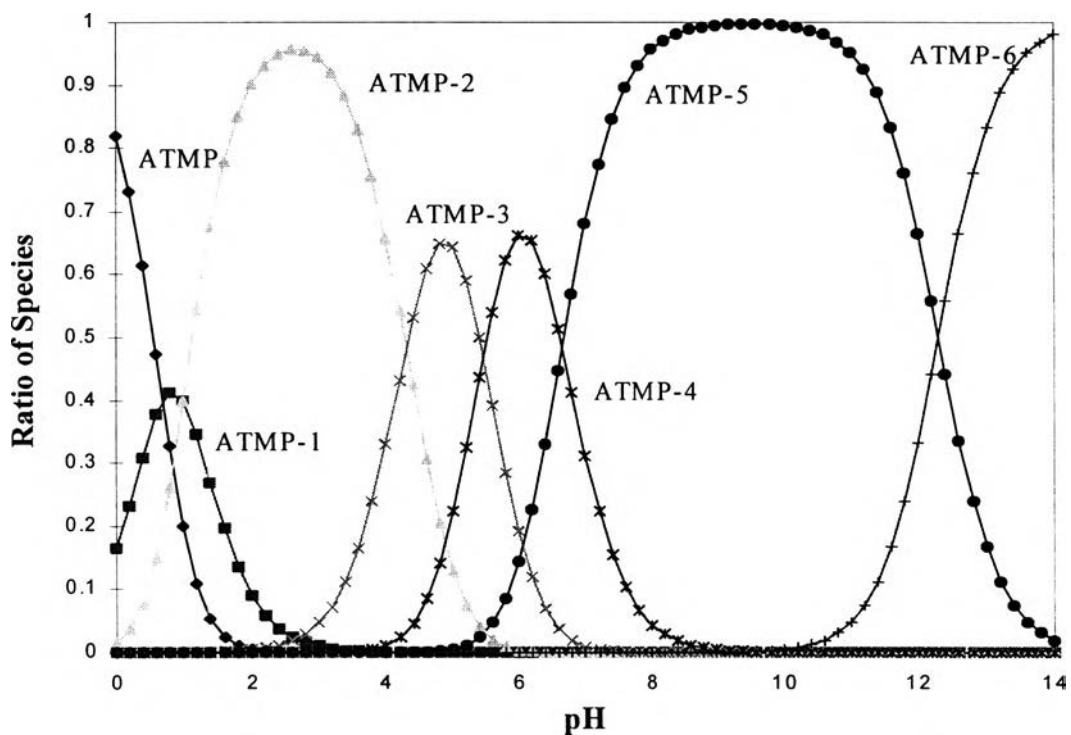


Figure 4.13 Effect of pH on the Deprotonation of ATMP and the Resulting Species Composition.

At a pH of 1.5, the ATMP molecules have deprotonated 1 and 2 hydrogens. That indicates one calcium cation can potentially react with one ATMP molecule and form a 1:1 calcium-ATMP precipitate which is proved by the result (see Table 4.1). A 2:1 calcium-ATMP precipitates are showed apparently by this phenomenon similar as 1:1 calcium-ATMP precipitate. From the experimental results, at a pH of 4.0, 4.5 and 6.0 (a precipitating molar ratio was 1:1), 2:1 calcium-ATMP precipitates were formed at this conditions because there were suitable species for forming this

type of precipitates. Also, at pH of 7.0 or above, 3:1 calcium-ATMP precipitate are possibly formed because all ATMP molecules have deprotonated 5 and 6 hydrogens which three calcium cations have potential to attach with one ATMP molecule.

4.1.3.2 The Effect of Calcium on the Resulting Titration

During titration, the solution's pH was decreased while Ca^{++} solution was introduced into the ATMP solution. That means the calcium cations are replaced hydrogen in hydroxy group, and then hydrogens are deprotonated. Thus, it affects to decrease the pH in precipitating solution during titration. As shown in Figure 4.14, the upper curve is represented the titration curve between 0.1 M ATMP and 1.0 N KOH without calcium cation. The lower titration curves are compounded with 0.011 M and 0.05 M calcium cations. As shown in Figure 4.14, the curves included with calcium cations have an effect on the pH of solution. Due to the batch synthesis experiment (Part 4.1), the solution's pH was adjusted to a desired pH, and then Ca^{++} solution was introduced into the system. The pH in solution was dropped to the lower curve at the same amount of KOH. The calcium cation has an effect to the titration curves when the pH in the system is higher. However, at a low pH the calcium cation is hardly affected to the changing of the titration curves in the system.

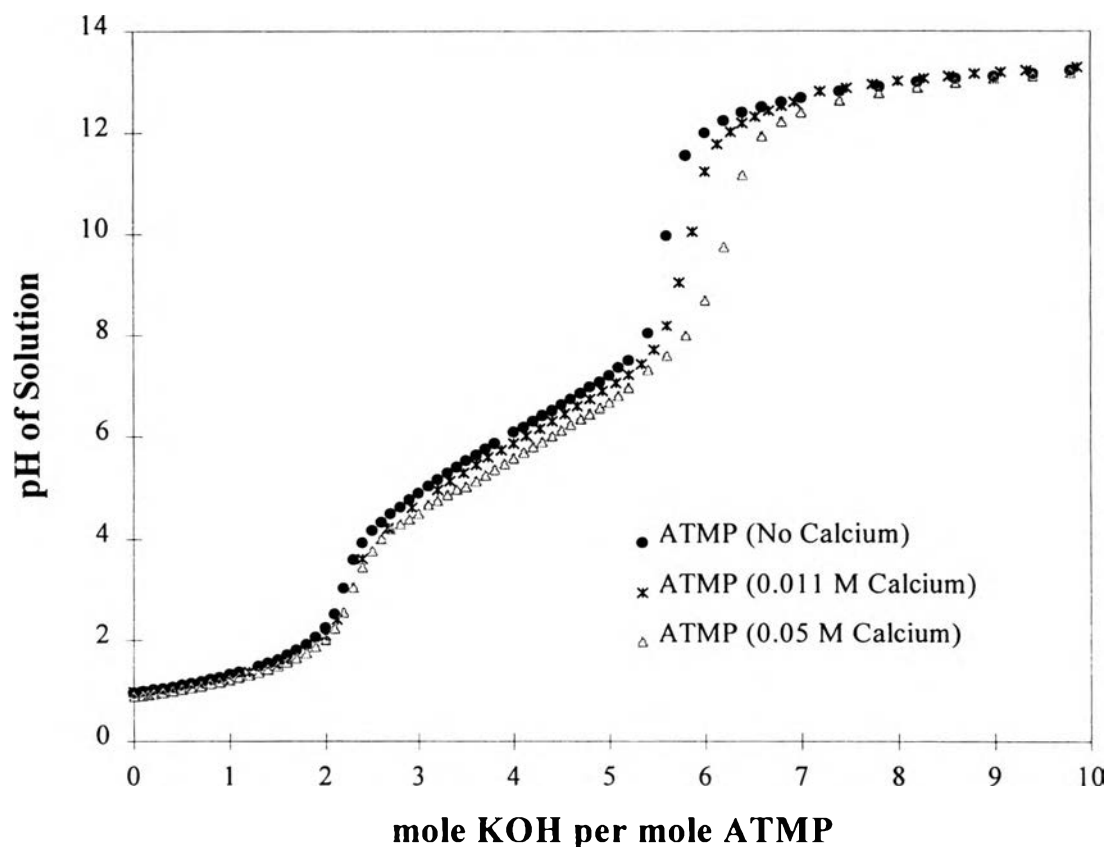


Figure 4.14 The Effect of Calcium in Solution on the Resulting Titration Curves of ATMP.

4.1.3.3 Precipitation of Ca-ATMP as Function of pH and Calcium Concentration

To better understand the effect of forming the precipitate, Figure 4.15 is shown the extreme conditions in forming sparingly calcium-ATMP soluble precipitates. The precipitation is dependent upon a function of scale inhibitor concentration, Ca^{++} ion concentration and solution's pH. The area above any curve is a precipitating zone which is equal or higher than the degree of supersaturation. The higher ATMP concentration is used, the lower precipitating pH is available for forming the precipitate. This

precipitation boundaries shown in Figure 4.15 were obtained by titration many solutions containing the prepared concentrations of Ca^{++} ions and ATMP with a 10 N KOH (Vetter, 1972). During titration, the pH meter was used for monitoring the pH values changed when the reaction was presented.

At a pH of 9.0 in Table 4.1, no precipitate is formed after titration is completed at a precipitating Ca/ATMP molar ratio of 1:1. As shown in Figure 4.15, at the higher pH in solution, the more amount of Ca^{++} ions is needed to form the precipitate at the same amount of ATMP concentrations.

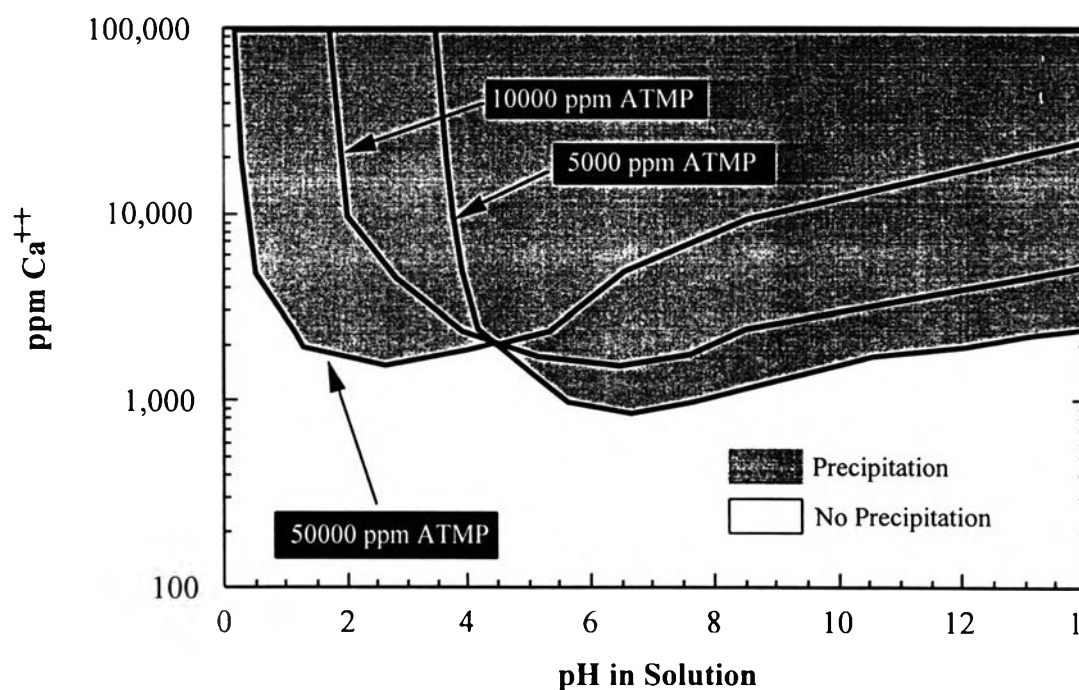


Figure 4.15 Precipitation of Ca-ATMP as Function of pH and Calcium Concentration.

4.2 Performance of Precipitate in Porous Media

The properties of calcium-ATMP precipitates are revealed from the characterization of precipitates described in part 4.1. There were three types of precipitates which were used to study the performance in porous media. Micromodel and Coreflood experiments were used as model for representing a porous medium.

First, the supersaturated solution of calcium-phosphonate was injected into the porous media and set it for a shut-in period. Then, the precipitate was formed. After shut-in period, the production was resumed, the precipitate was released back into the produced fluid concerning with the rate of phosphonate released and hence, the squeeze treatment lifetime.

The concentration of phosphonate in the produced fluid was monitored as a function of time and amount of produced fluid. The typical elution curves of three precipitates from a precipitation squeeze treatment are showed in Figure 4.16. The concentration of phosphonates declined rapidly at the beginning of elution and then became slowly at the long period. The higher degree of precipitate was formed, the longer release of phosphonate was presented. These results related with the solubility limit of precipitates which were shown in Table 4.1. The solubility concentrations of the 1:1, 2:1 and 3:1 precipitates were 1221, 453 and 241 ppm, respectively. The driving force for precipitate dissolution, $(C_s - C)$, of the 1:1 precipitate was greater than the 2:1 and 3:1 precipitates. Consequently, the dissolution rate of the 1:1 precipitate was highest.

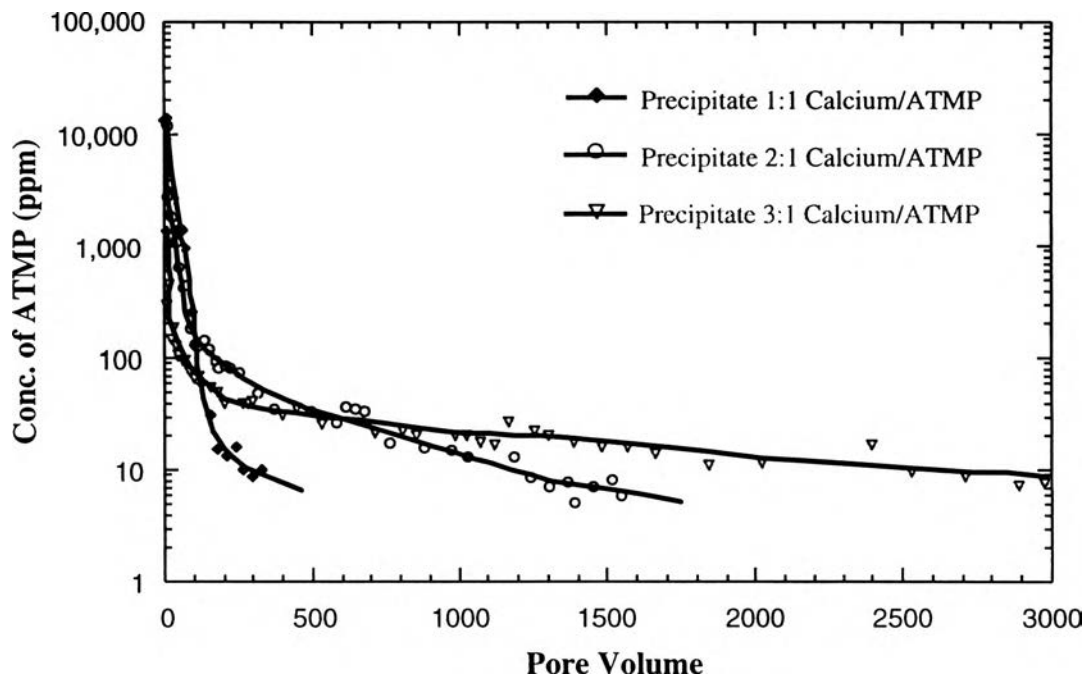


Figure 4.16 Effect of Precipitate Types of the Release of ATMP from Micromodel Experiment.

The observations suggest that because the 3:1 precipitate offers the slowest release of ATMP from porous media, this precipitate may be suited for phosphonate treatments in oilfield applications. However, the precipitate formed in the oilfield is dependent upon many conditions as above mentions such as a precipitating pH, degree of supersaturation, calcium/ATMP molar ratio in a precipitating condition etc. As knowing the conditions which the desired precipitate forms, oil producers can induce this desirable precipitate into porous media and enhance phosphonate treatments in oil production system.

4.2.1 Description of the 1:1 Calcium-ATMP Precipitate Released from Model

A typical elution curve resulting from a precipitation squeeze treatment of 1:1 calcium-ATMP precipitate is illustrated in Figure 4.17. Four distinct regions of the elution curve have been identified as below.

Region 1) an initial flat region : the precipitate compacted into pore throat. The saturated calcium-ATMP solution initially contacted with precipitate was swept from the micromodel, resulting the high ATMP concentration seen in the elution curve during the beginning range of pore volume. (see Figure 4.18)

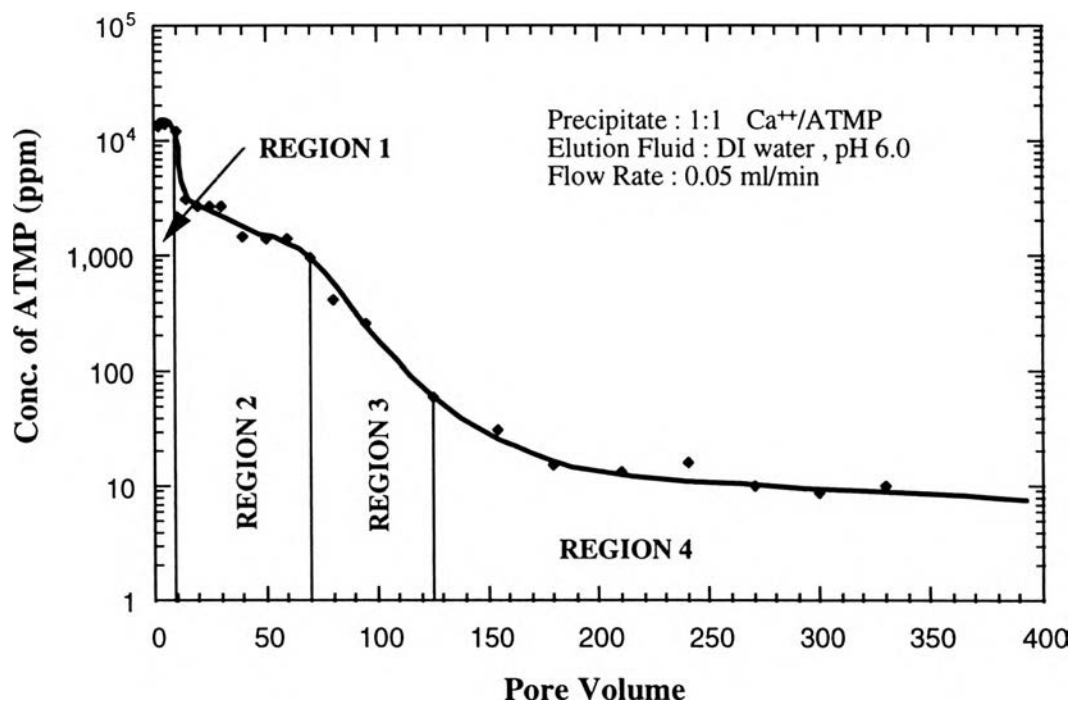
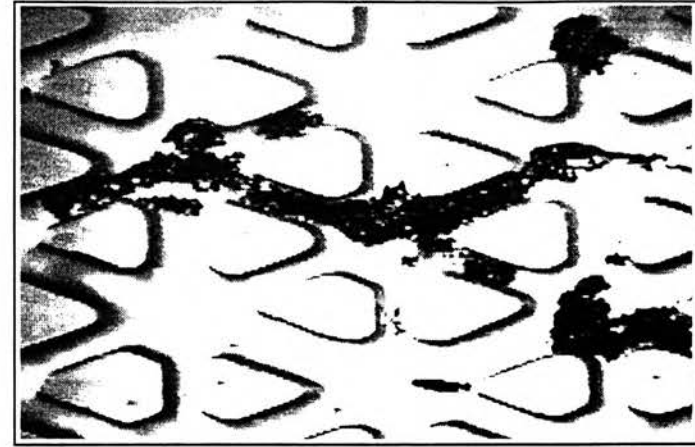


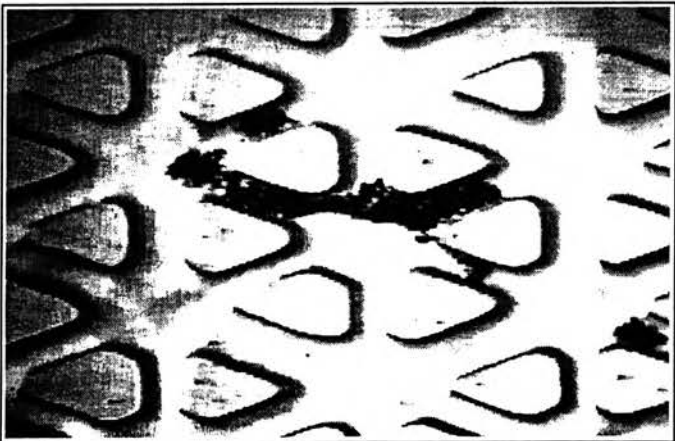
Figure 4.17 Elution Curve Resulting from the Dissolution of a 1:1 Calcium-ATMP Precipitate in Porous Media.



Region 1 The saturated Ca-ATMP solution attached with precipitates was swept from a micromodel.



Region 2 The precipitates situated in pore bodies were dissolved by hydrodynamic dissolution.



Region 3 The remaining precipitates were dissolved by both external/internal hydrodynamic dissolution.



Region 4 The dissolution of precipitates was slowly which they were shrunk into the pore throat.

Figure 4.18 Release Regimes of 1:1 Ca^{++} - ATMP Precipitate from a Micromodel .

- Region 2) a slowly declining region :** the precipitate in pore throat was dissolved by external hydrodynamic dissolution. The precipitate was exposed to the fluid flowing and dissolved the precipitate loosely packed in pore bodies. (see Figure 4.18)
- Region 3) a more declining region :** the precipitate was dissolved by both external and internal hydrodynamic dissolution. The remaining precipitate in pore bodies was easily dissolved and shrunk rapidly. (see Figure 4.18)
- Region 4) a long tailing region :** the precipitate was extended and situated into the pore throat. The dissolution of precipitate was so slow which had shown in the tail of elution curve. The elution curve was rather constant at which was above the minimum effective concentration. (see Figure 4.18)

4.2.2 Description of 2:1 Calcium-ATMP Precipitate Released from Model

The elution curve of 2:1 precipitate is described in Figure 4.19. The curve is divided by two regions (also see Figure 4.20).

- Region 1)** In this region, saturated calcium-ATMP solution initially contacted with precipitate was swept from the micromodel. The curve of this region rapidly declines, hydrodynamic dissolution of precipitate extending outward into the pore bodies took place. The precipitate was rapidly dissolved because of the high surface area of precipitate exposed to the flowing fluid.

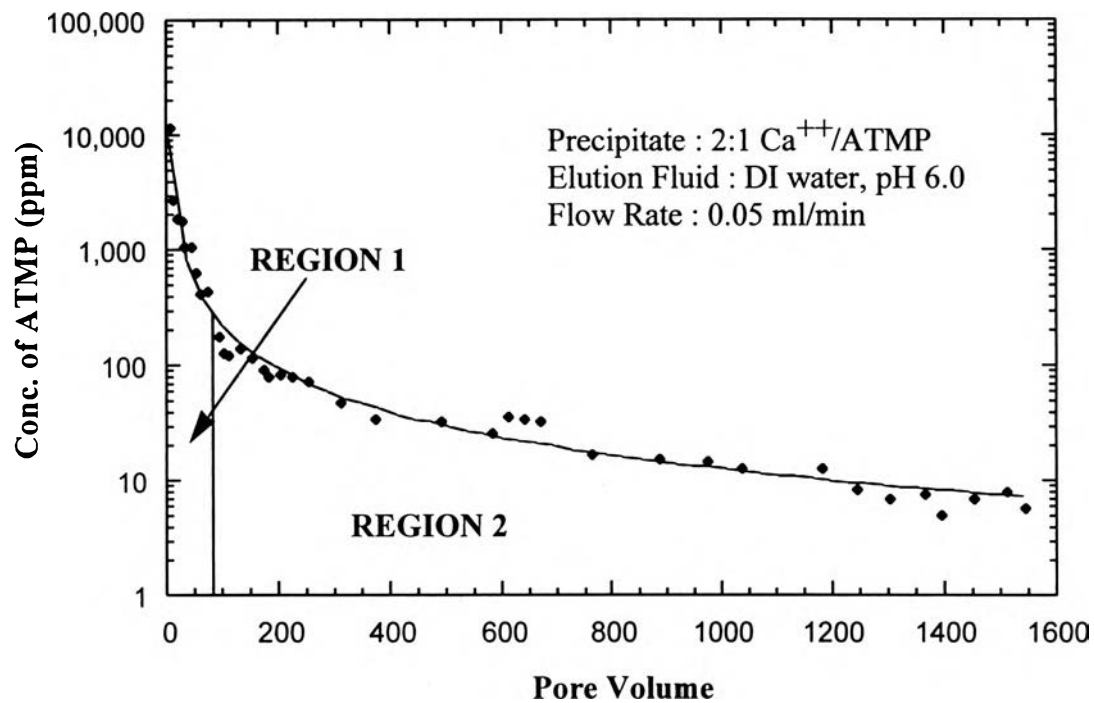
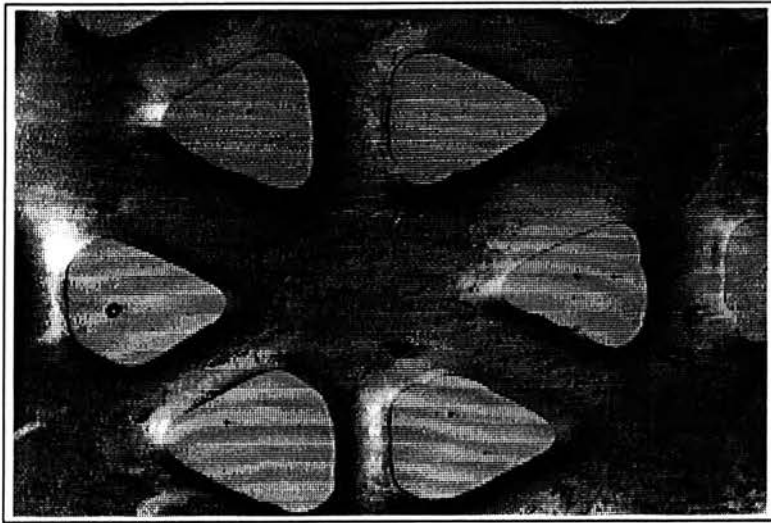
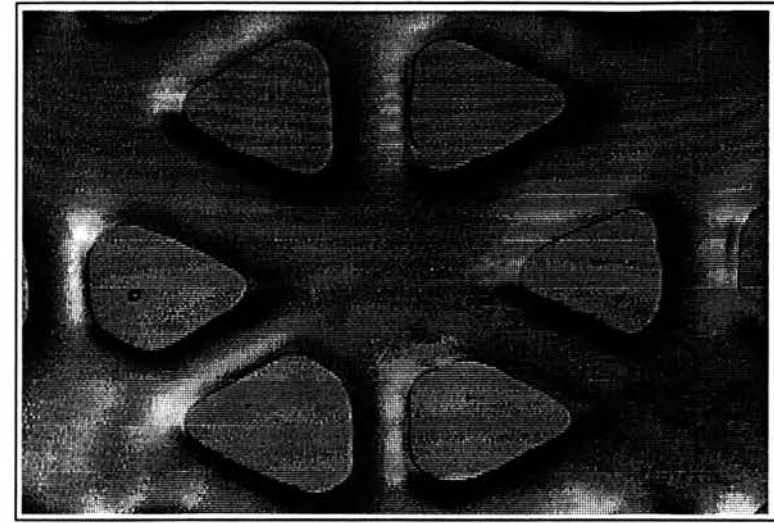


Figure 4.19 Elution Curve Resulting from the Dissolution of a 2:1 Calcium-ATMP Precipitate in Porous Media.

Region 2) The remaining precipitate still packed in the pore throat. The rate of dissolution of a 2:1 precipitate was slightly declined because of the low solubility. Squeeze lifetime of a 2:1 precipitate was longer than 1:1 precipitate.



Region 1 The saturated calcium-ATMP solution initially contacted was swept and dissolved by hydrodynamic dissolution.



Region 2 The remaining precipitate was packed in pore throat and dissolved slowly.

Figure 4.20 Release Regimes of 2:1 Ca^{++} -ATMP Precipitate from a Micromodel.

4.2.3 Description of 3:1 Calcium-ATMP Precipitate Released from Model

The 3:1 precipitate has the same characteristic elution curve as a 2:1 precipitate (see Figure 4.21) but differs at the performance of dissolution and squeeze lifetime. The elution curves of the 3:1 precipitate can be divided by two regions.

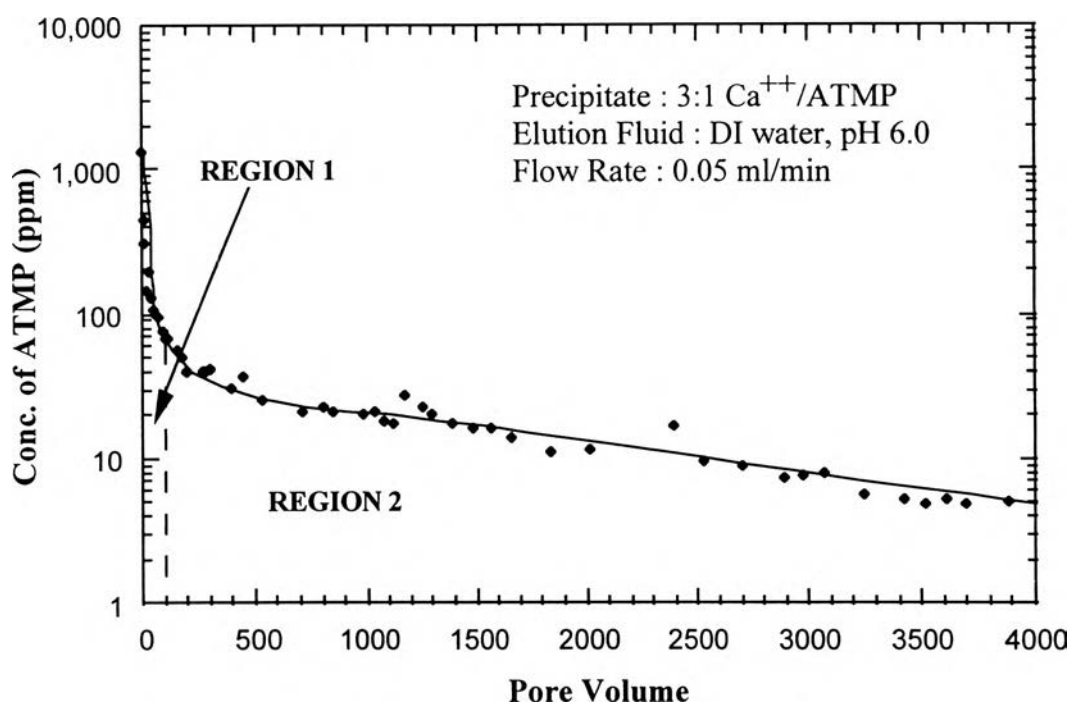


Figure 4.21 Elution Curve Resulting from the Dissolution of a 3:1 Calcium-ATMP Precipitate in Porous Media.

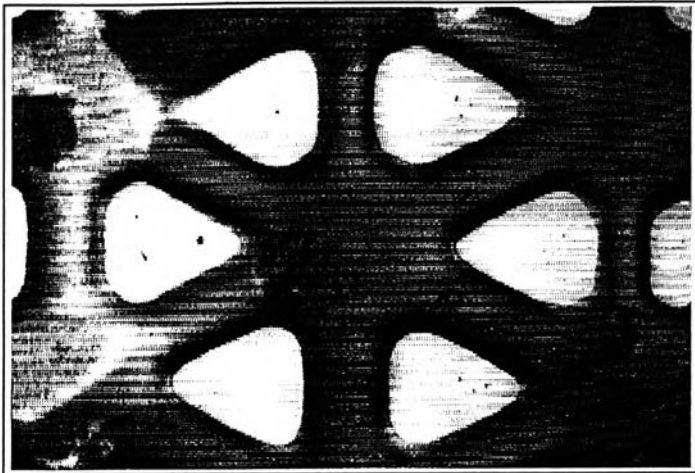
Region 1) In this region, saturated calcium-ATMP solution initially contacted with precipitate was swept from the micromodel. Thus, the high concentration of ATMP monitored was shown in the elution curve. Then, the curve of this region rapidly declines,

hydrodynamic dissolution of precipitate extending outward into the pore bodies took place (see Figure 4.22). The precipitate was rapidly dissolved because of the high surface area of precipitate exposed to the flowing fluid.

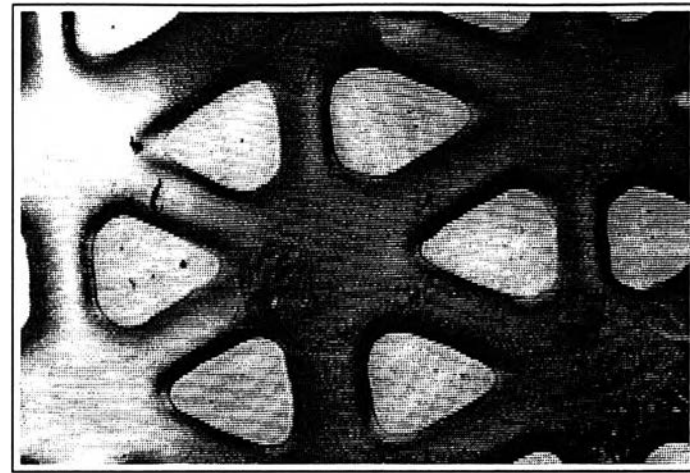
Region 2) Because of low solubility of a 3:1 precipitate, the elution curve shown in Figure 4.21 was extremely slow dissolution. At a long period of dissolution, precipitate situated in a porous medium mostly became to crystal form and packed strongly (see Figure 4.22). Thus, the precipitate was mainly dissolved by hydrodynamic of fluid flowing around the spherical particles.

These distinct elution curves were mirrored to represent the types of precipitates which had the distinct solubilities. The 1:1 precipitate had four regimes in dissolution which differed from the 2:1 and 3:1. With XRD results, the 1:1 precipitate had a form of crystalline but the 2:1 and 3:1 precipitates had a form of amorphous. Also, the results obtained by the solubility limits of the precipitates supported that the 1:1 precipitate had the highest solubility and fastest approach to the equilibrium comparing with other two precipitates. Thus, the releasing rate of the 1:1 precipitate from a porous media was higher than the other two.

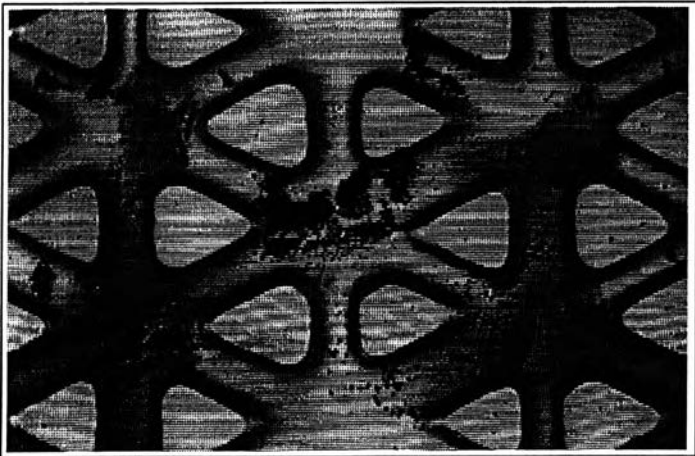
In the actual oilfield, during the production is resumed, the squeeze lifetime is a major factor of judgement with which precipitates are appropriate in each oilfield. The minimum effective concentration which is effective on inhibition of scale formation is around 5-20 ppm. Since the concentration of phosphonate drops below this effective concentration, the resqueeze is allowed in the field.



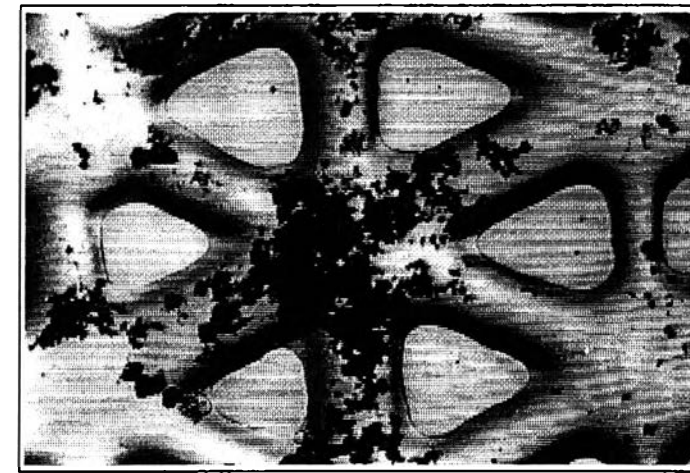
Region 1 The precipitate initially situated in a micromodel.



Region 1 The saturated Ca-ATMP solution was swept from a micromodel.



Region 2 The precipitates were slowly dissolved.



Region 2 The precipitates were developed to the crystal form and extremely slow dissolved.

Figure 4.22 Release Regimes of 3:1 Ca^{++} - ATMP Precipitate from a Micromodel.