CHAPTER IV
RESULTS AND DISCUSSION

4.1 Batch synthesis and characterization

The experiments on batch synthesis were performed by systematically varying the pH of precipitate solution and settling temperature. The experimental data are given in Appendix. Each of precipitate produced was subsequently characterized as described below.

4.1.1 Effect of pH on precipitate molar ratio

The pH of precipitate solution has a significant effect on bonding between calcium and DTPMPA and so it affects the properties of precipitates produced. The methodology for this study was to increase pH from 3 to 12 while holding both molar products. After pH decreased as a result of precipitation, KOH powder was added to the solution to maintain pH at the selected value. As shown in Figure 4.1, the effect of the solution pH on the composition of precipitates can be clearly observed. As the pH changed from 3 to 6, the precipitate molar ratio increased almost linearly. This phenomena can be simply explained that as the pH increases, the solution equilibrium shiftes resulting in increasing the number of hydrogen deprotonated from each DTPMPA molecule (see pKa values in Figure 4.2). As a result, the calcium atoms have more reacting sites on each DTPMPA molecule at higher pH which increases the Ca/DTPMPA molar ratio of precipitates. At pH ranging from 6 to 8, the Ca/DTPMPA molar ratio of precipitate was relatively constant about 1:3.
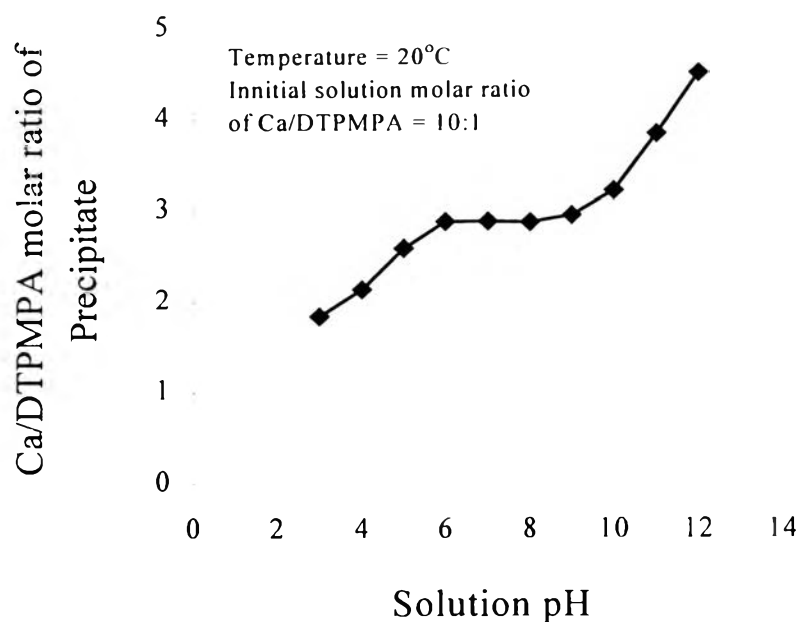
Figure 4.1   Effect of solution pH on the Ca/DTPMPA precipitate molar ratio.

This is due to the pKa values and it shows that at pH 6 to 8 fraction of species did not change much (see Figure 4.2). At this range of pH, the DTPMPA molecules are able to be protonated about 5 to 7 hydrogens. This indicates that 3 calcium cations can potentially react with one DTPMPA molecules. When further raising in the solution pH from 8 to 12, the fraction of species increased and the number of deprotonated hydrogen increases drastically. Therefore a significant increase in the Ca/DTPMPA molar ratio of precipitates was obtained.
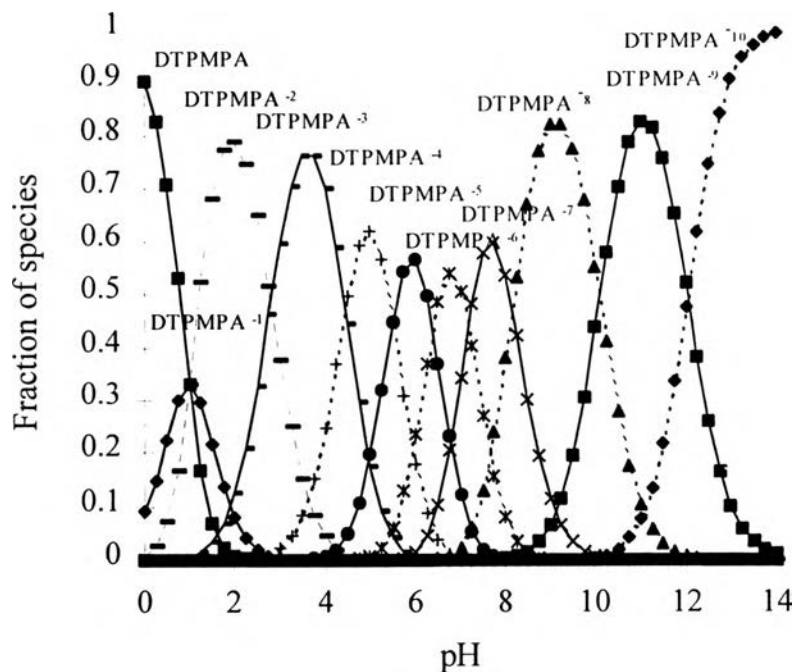
Figure 4.2   Effect of pH on deprotonation of DTPMPA and resulted species
composition.

Although the initial solution molar ratio of Ca/DTPMPA was
kept constant at 10:1, the Ca/DTPMPA molar ratio in precipitates changed in
the range of 2 to 4.5. This phenomena can be explained that the excess calcium
is able to inhibit the chelation chemistry of this system, then the solution
equilibrium is shifted and resulting in a reduction of pKa values.

4.1.2   Effect of temperature on Ca/DTPMPA molar ratio

In the real reservoir, temperature varies in the wide range which
affects the formation of scale inhibitor precipitates. At higher temperature, the
precipitate molar ratio is higher. Figure 4.3 shows the effect of temperature on
the Ca/DTPMPA molar ratio of precipitate under different solution pH. As can
be seen from Figure 4.3, an increase in temperature results in a significant
increase in the Ca/DTPMPA molar ratio of precipitates. The effect of

temperature increasing from 20° to 30° C was much greater than the one increasing from 30° to 60° C. It can be explained that when temperature increases, the thermodynamic chemical bond will be loosened and easier to break resulting in the calcium ion capable to attach with posphorous atom instead of hydroxide. This indicates that temperature is on significant factor involving the precipitation process.
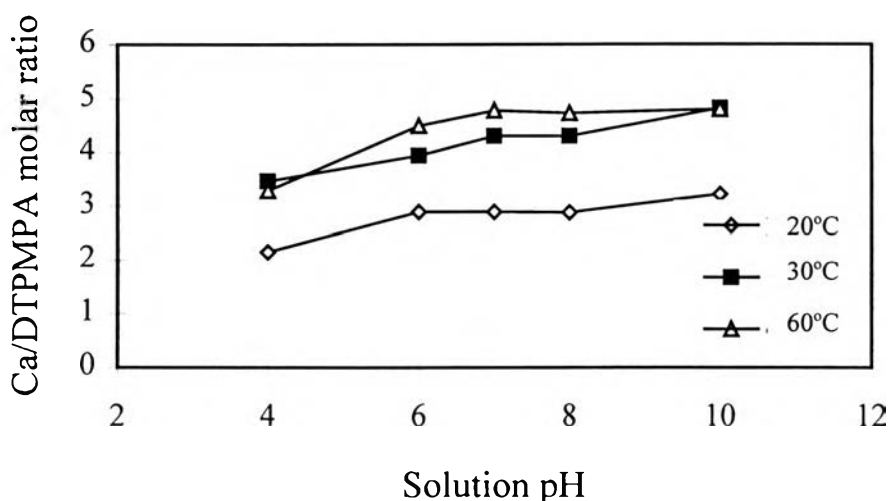
Figure 4.3 Effect of settling temperature on the Ca/DTPMPA molar ratio under different solution pH at the initial solution molar ratio of Ca/DTPMPA = 10:1.

4.1.3 Effect of molar ratio on precipitate morphology

In order to obtain better understanding about the properties of precipitates, their morphology was studied by using a scanning electron microscope (SEM). Figure 4.4 shows the morphological structures of three different precipitates. The precipitate at molar ratio of 2:1 was less crystaline than that at the molar ratio of 2.9:1 because the crystallinity increased by

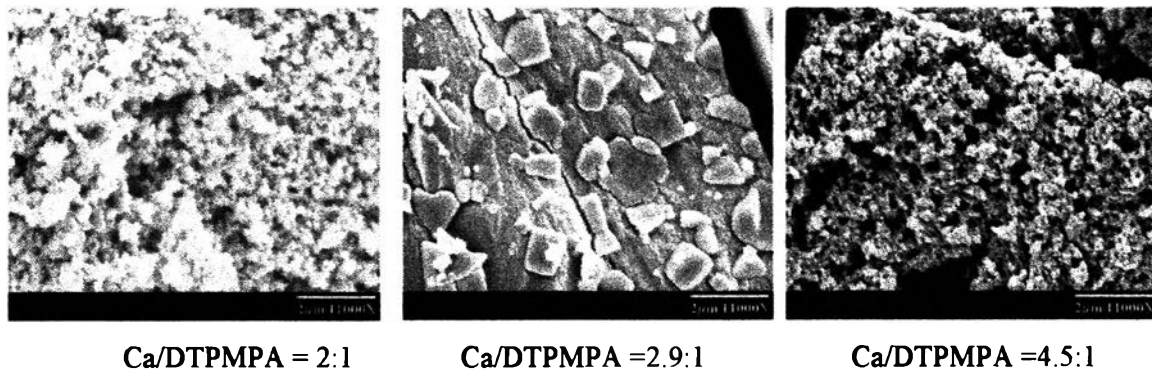Ca/DTPMPA = 2:1   Ca/DTPMPA =2.9:1   Ca/DTPMPA =4.5:1

Figure 4.4   Morphological structures of distinct Ca/DTPMPA precipitates at three different Ca/DTPMPA molar ratio.

molar ratio. When molar ratio increased to 4.5:1, the finer crystalline structure occurred. The X-ray diffraction patterns of these three precipitates clearly confirm that the higher molar ratio results in more crystallinity (see Figure 4.5).
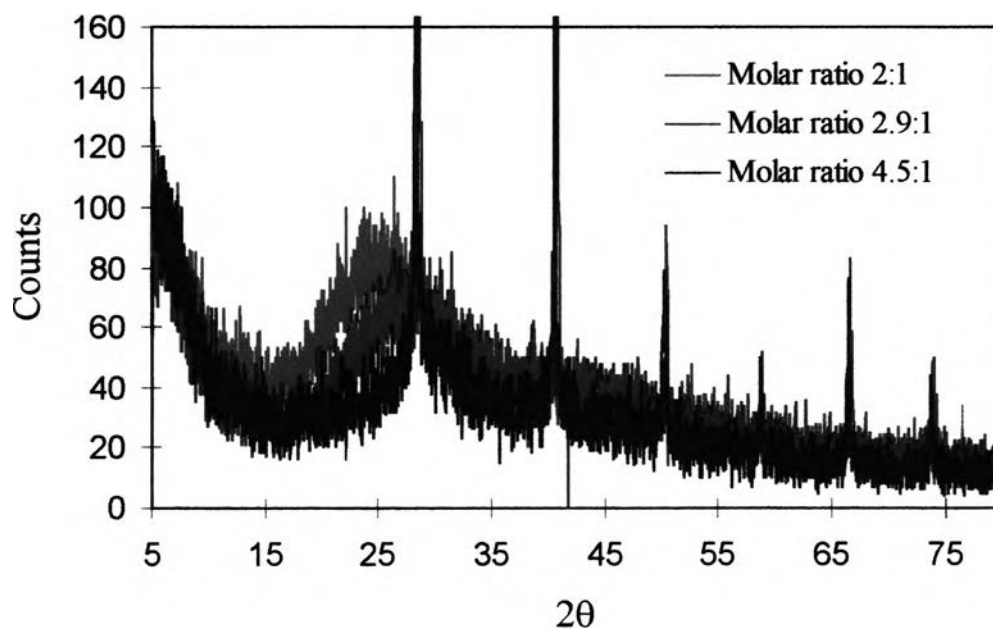

Figure 4.5   X-ray diffraction patterns of three different Ca/DTPMPA molar ratio precipitates.

4.1.4 Effect of molar ratio on equilibrium solubility

Table 4.1 shows that the precipitates formed at molar ratio of 2:1 has the highest equilibrium solubility concentration while the precipitate formed at molar ratio of 4.5:1 has the lowest solubility since the more crystalinity at the higher molar ratio results in the lower solubility. At higher molar ratio, precipitate is heavily packed with dense calcium ions on DTPMPA then it is difficult to dissolve compared with the loose pack of less Ca/DTPMPA precipitates which is formed at lower pH. In addition, high molar ratio of precipitates formed at slower rate than that at low molar ratio, which gas channel may appear and increased surface area. At any given Ca/DTPMPA molar ratio, the equilibrium solubility of the precipitate did not vary with pH.

Table 4.1   Effect of dissolving liquid pH on the equilibrium solubility and precipitate molar ratio

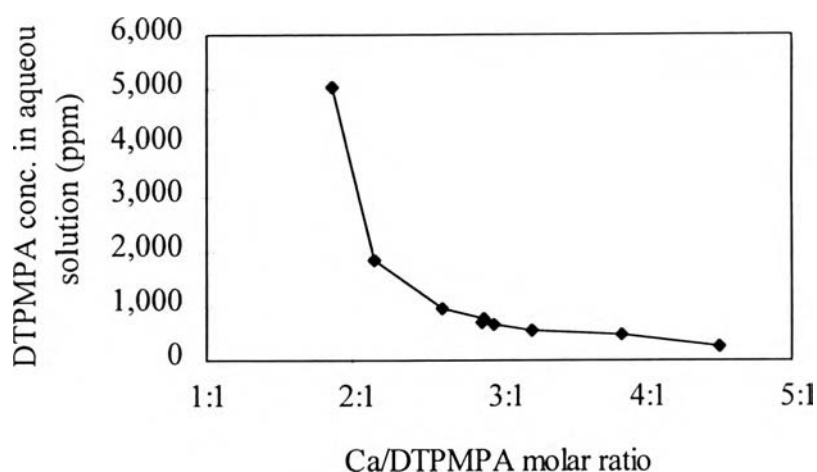| Precipitate molar ratio (Ca : DTPMPA)	Dissolving liquid pH	Equilibrium solubility concentration, ppm
1.9:1	4	5508
	7	5309
	10	4987
2.9:1	4	670
	7	667
	10	658
4.5:1	4	286
	7	269
	10	266

Figure 4.6   Effect of Ca/DTPMPA molar ratio on equilibrium solubility at solution pH 7.

These equilibrium solubility data is very useful for oil field application. This is because of the equilibrium solubility limit can indicate the released rate of phosphonate scale inhibitor back to the production system and control the squeeze lifetime. For example of DTPMPA, the effective concentration that can inhibit scale formation is 10 ppm. When the scale inhibitor dissolves in production fluid at equilibrium, then every molar ratio was effective, but if with high equilibrium solubility it meaned the loss of inhibitors in the produced fluid.

The precipitate having higher molar ratio has a higher equilibrium solubility than the precipitate having lower molar ratio. From the results, it indicated that the equilibrium solubility was also dependent on the dissolving liquid pH.

4.2 Precipitate behavior in micromodel

For dissolution of precipitates as described in the batch synthesis, the molar ratios of the Ca/DTPMPA precipitate depended on the solution pH. This section will focuses on studying the displacement and subsequent release of these three types of precipitates from this simulated porous medium and how these precipitates formed within the porous medium. The results obtained can indicate the squeeze lifetime of this inhibitor.

4.2.1 Effect of precipitate molar ratio on the release process

For the precipitate molar ratio of 2:1, the Ca/DTPMPA precipitate was initially contacted with dissolving fluid, it was swept at early period caused by the loose pact between the particles and the glass surface (see Figure 4.7 and 4.8). As can be seen in Figure 4.8, it appears precipitate agglomerates at pore body (pore volume = 45) and the mixed of small precipitates and the fibrous ones were formed. As elution fluid volume increased, more precipitates were dissolved with the injected fluid. Due to small amount of precipitates left in micromodel, the phosphate concentration in the effluent fluid gradually decreased with a very slow rate.

In case of Ca/DTPMPA molar ratio of 2.9:1, the precipitates forming in small crystal shape appears to agglomerate tightly at the pore body as shown in Figure 4.10. Figure 4.5 shows a relatively faster dissolution rate of the precipitate of 2.9:1 Ca/DTPMPA molar ratio in comparison to the 2:1 Ca/DTPMPA precipitate. Similar results were also obtained for the precipitate having the Ca/DTPMPA molar ratio of 4.5:1 (see Figure 4.11 and 4.12). For Ca/DTPMPA molar ratio 4.5:1, the precipitates those small crystals and fibrous ones, were formed in the mixed type of molar ratio 4 and 5. From the

elution curve, the slowly decreasing rate of phosphate concentration showed the high crystallinity of precipitates.
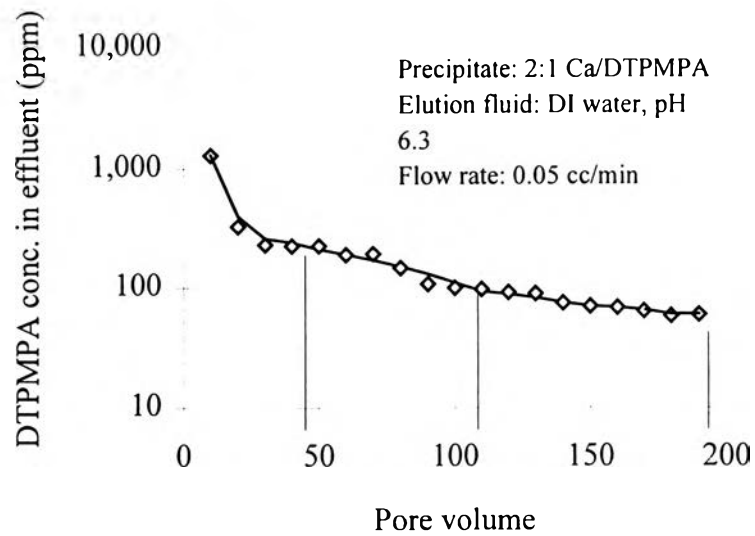

Figure 4.7   Elution curve resulting from dissolution of 2:1 Ca/DTPMPA precipitate in micromodel.

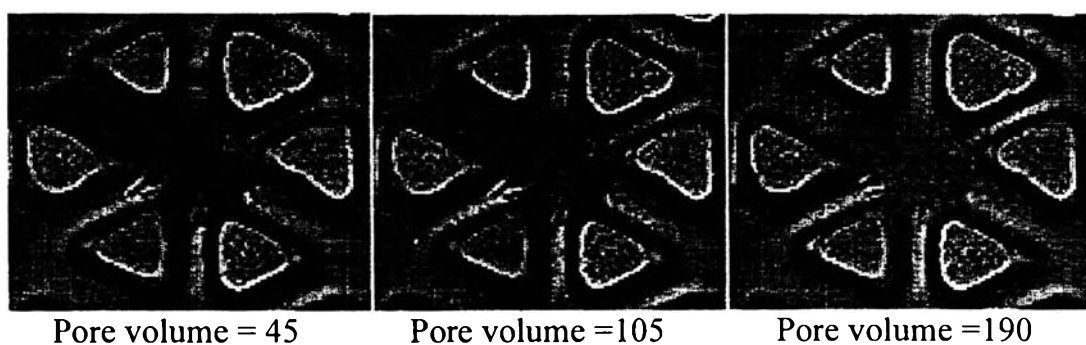Pore volume = 45   Pore volume =105   Pore volume =190

Figure 4.8   Sequential release of 2:1 Ca/DTPMPA precipitates from micromodel.
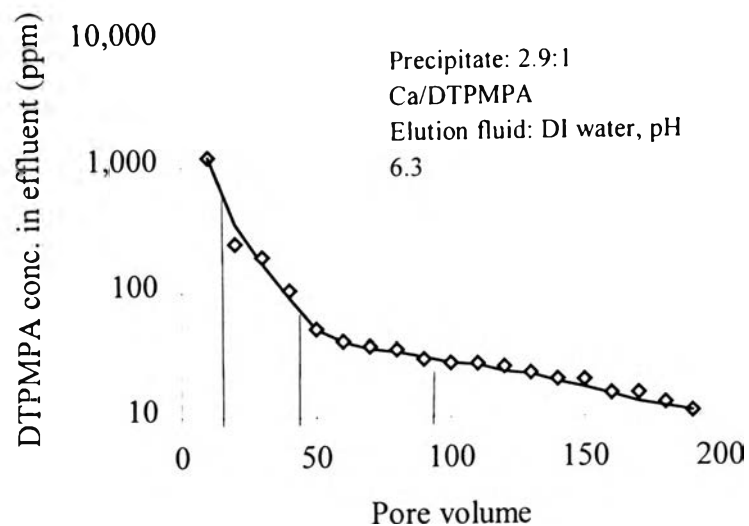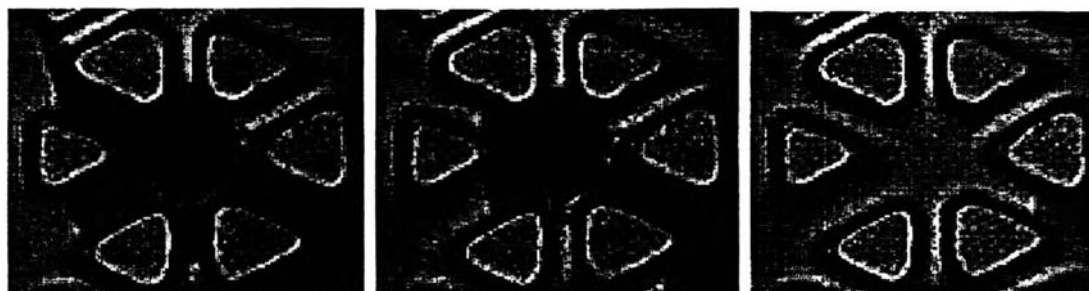
Figure 4.9   Elution curve resulting from the dissolution of a 2.9:1 Ca/DTPMPA precipitate in micromodel.

Pore volume = 15   Pore volume = 45   Pore volume = 90

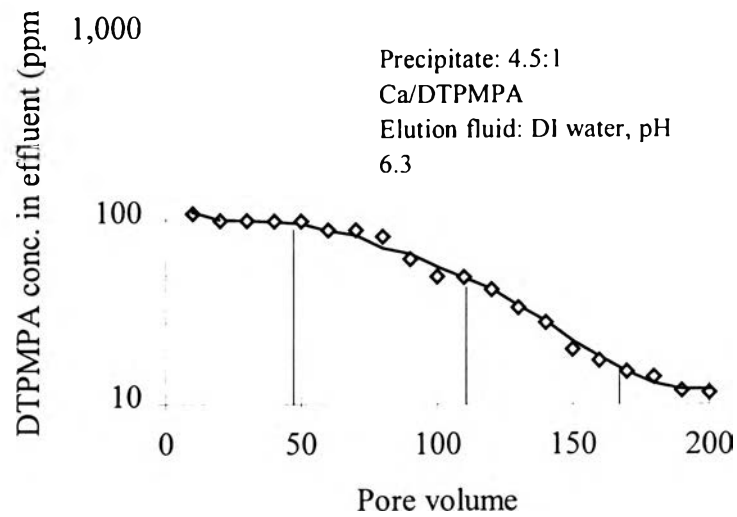Figure 4.10   Sequential release of 2.9:1 Ca/DTPMPA precipitates from micromodel.

Figure 4.11 Elution curve resulting from the dissolution of a 4.5:1 Ca/DTPMPA precipitates in micromodel.

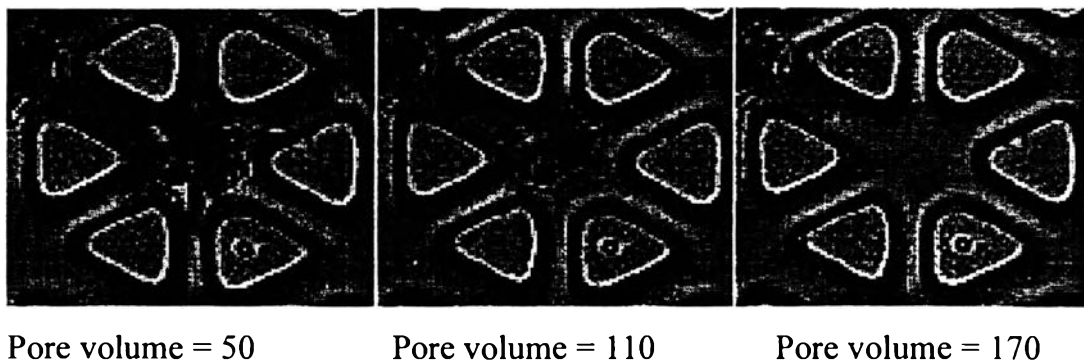Pore volume = 50   Pore volume = 110   Pore volume = 170

Figure 4.12 Sequential release of 4.5:1 Ca/DTPMPA precipitates from micromodel.

Figure 4.13 shows the effectiveness of three different precipitates releasing from the micromodel. The Ca/DTPMPA molar ratio 2:1 was eluded in large amount (area under the graph) compared with the molar ratios of 2.9:1 and 4.5:1. The results agree very well with the experimental results of the solubility. It can be said that the precipitates at 2.9:1 and 4.5:1 molar ratios give long squeeze lifetime of scale inhibitors (at the same amount of phosphate).
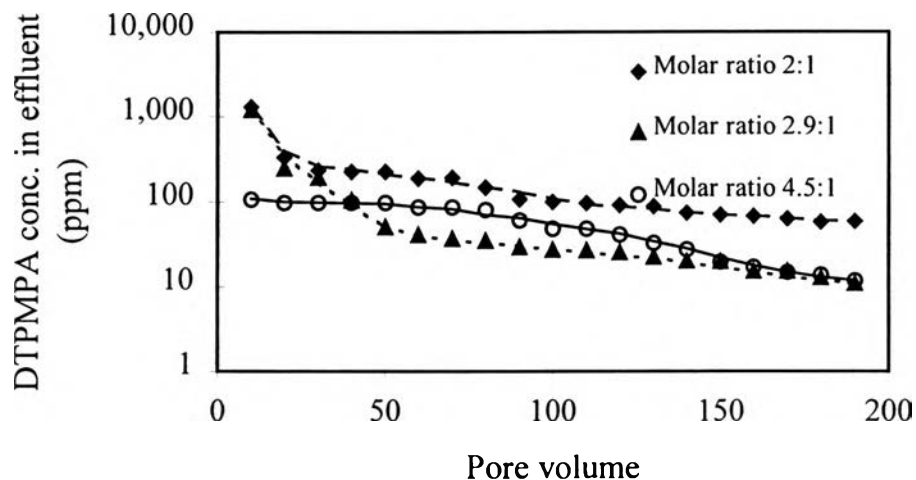

Figure 4.13 Effect of precipitate molar ratio on the release of DTPMPA in the micromodel experiment.

4.2.2 Effect of dissolving liquids on the DTPMPA release rate in micromodel

In an oil field, water-flooding is commonly applied to retain pressure gradient in the reservoir. The injected liquid conditions can directly affected the dissolution rate of scale inhibitors. The liquid pH is one of the important factors influencing the squeeze lifetime. As shown in Figure 4.14, the liquid pH 10 gives the longest squeeze lifetime comparing with dissolving liquid pH 6.3 (DI water), and the shortest squeeze lifetime was found at pH 2. These results can be explained that the phosphonate dissolves more in acidic

solution rather than alkali solution. In oil field application, acidization is one of the pretreatment techniques to penetrate the rock and make hole for oil flow path. After this process is used, large amount of scales comes out and the reservoir becomes more acidic than usual reservoir. The squeeze treatment is then applied to eliminate these scales, then more scale inhibitors should be added in order to retain the squeeze lifetime.
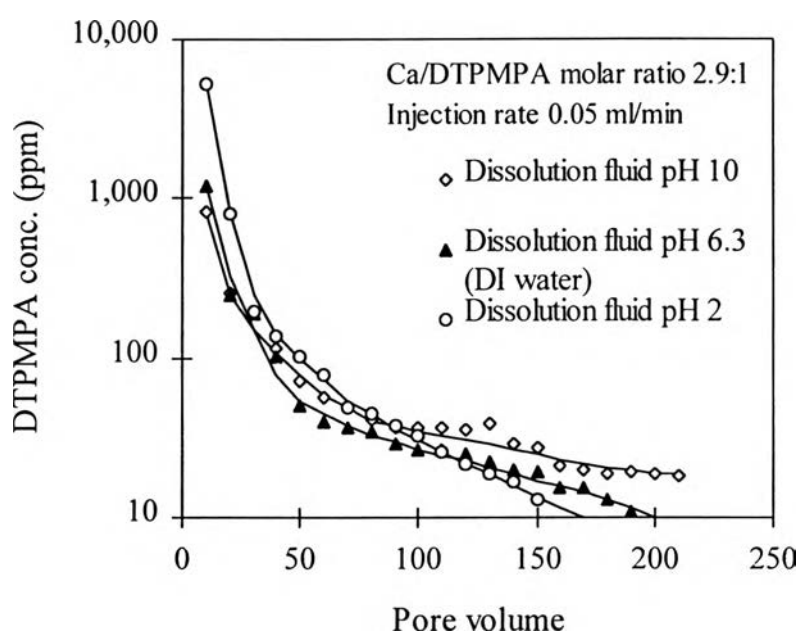

Figure 4.14   Effect of dissolving liquid pH on the DTPMPA release rate in micromodel.

4.3   Comparison effectiveness of different phosphonates

In typical squeeze treatment, phosphonate inhibitors of useful. amino tri(methylene phosphonic acid, ATMP), 1-hydroxy ethylidene (1,1-diphosphonic acid, HEDP), and diethylene triamine penta (methylene phosphonic acid, DTPMPA) are widely used since they are highly effective in

scale controlling. These chemicals have different properties as shown in Table 4.2.

Table 4.2   Typical properties of DEQUEST® phosphonate

Product	Amminotri (methylene phosphonic acid)	1-Hydroxy ethylidene (1,1-diphosphonic acid)	Diethylene triamine penta (methylene phosphonic acid)
Abbreviation	ATMP	HEDP	DTPMPA
Molecular weight	299	206	573
$CaCO_3$ inhibition	Excellent	Excellent	Very good
$CaSO_4$ inhibition	Good	Poor	Very good
Calcium Compability	Good	Poor	Good
Application notes	Good for general purpose, cost-effective scale inhibitors	Noted for its excellent $CaCO_3$ scale inhibition and chlorine stability	Good general purpose scale inhibitor, especially against barium sulphate
List price (CIF) ($/kg)	1.5	2.2	2.6

The effectiveness of three different scale inhibitors of ATMP, HEDP and DTPMPA are compared experimentally using the micromodel as shown in Figure 4.15. ATMP has the highest release rate while HEDP has the lowest release rate. Foe this study, the release rate of DTPMPA was found to be slightly slower than that of ATMP. It can be concluded that for Calcium-type

scale, HEDP is the most effective scale inhibitor. It can give a very low minimum concentration at about 5 ppm and provide a much longer squeeze lifetime in comparison to the others. However, one must bear in mind that if
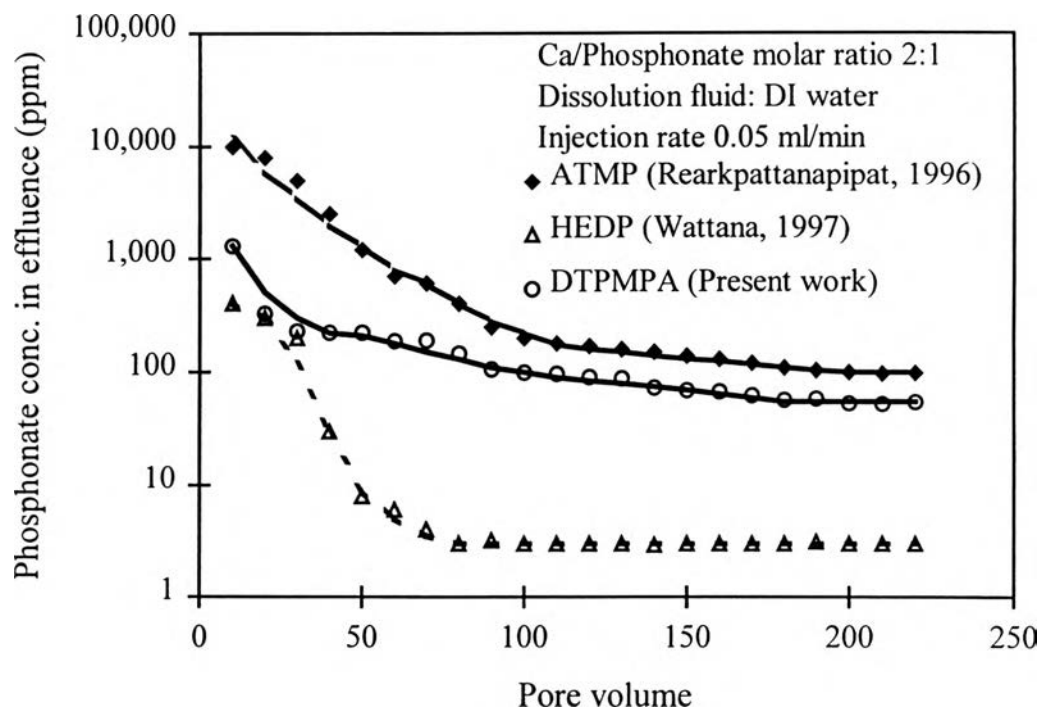

Figure 4.15   Effectiveness of phosphonate release of different types of phosphonates in micromodel.

the aqueous solution in formation contains other salts such as $BaSO_4$, $MgSO_4$ etc, HEDP will not be the best scale inhibitor. Other type or combination of scale inhibitors should be considered to apply for the squeeze treatment.