CHAPTER V
CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In this work, there were two main parts involving precipitation batch synthesis and batch dissolution experiment. Precipitation batch synthesis composed of the formation of Ca-ATMP precipitates, Mg-ATMP precipitates and Ca-ATMP precipitates with the presence of magnesium ion. All precipitates were synthesized under nitrogen atmosphere by simple titration technique and then analyzed for precipitate composition by AAS and Hach technique. The morphologies and crystallinity of the resulting precipitates were further examined by SEM and XRD, respectively. Finally, the resulting precipitates were used in batch dissolution experiments by using a rotating disk reactor for evaluating the dissolution performance and proving the hypothesis between co-precipitation and complex precipitation. From the experimental results, they can be concluded as below.

1) The precipitating solution pH significantly affected the precipitate composition in terms of a molar ratio of divalent cations to phosphonate. This molar ratio increased with increasing the precipitating solution pH because of more reacting sites for reacting with divalent cations at higher pH values.

2) Three distinct types of Ca-ATMP precipitates, 1:1, 2:1 and 3:1 were formed at precipitating solution pHs of 1.5, 4 and 7, respectively. The morphologies and XRD patterns of 1:1 Ca-ATMP precipitates demonstrated sheet particles and crystalline in nature, while 2:1 and 3:1 Ca-ATMP precipitates were spherical particles and amorphous structure. These results were good agreement with the previous work (Rerkpattanapipat, 1996).

3) 1:1 Mg-ATMP precipitate was formed at the same precipitating solution pH (pH=1.5) but the formation of this precipitate was more difficult than the formation of 1:1 Ca-ATMP precipitate due to its high solubility product (Ksp). Sheet particles and crystalline form were clearly observed from this precipitate as well.

4) The calcium to ATMP molar ratio in the resulting precipitate decreased with increasing the total magnesium concentration in the system. This phenomenon implied that the reacting sites of ATMP molecule available for bonding with calcium ion decreased because of the replacement by magnesium ion.

5) An increase of the magnesium concentration in the system (total Ca/Mg molar ratio in the system decreased) resulted in an increase of magnesium content found in the resulting precipitates. It was evident that when total magnesium concentration increased, the equilibrium reaction was shifted to the direction whereas can reduce magnesium concentration in the solution resulting in more Mg-ATMP precipitates.

6) As an increase in ionic strength resulted from increasing the total magnesium concentration in the system, the equilibrium acid constant (pKa') was significantly decreased causing in a shift of deprotonation curve (shift to the left hand side) of ATMP molecule giving more deprotonated hydrogen atom. Consequently, the precipitate molar ratio increased.

7) No precipitates were observed at solution pH of 4 and ionic strength of around 8 M. It was due to the shift of deprotonation curve producing much more unstable dominant species as $ATMP^{5-}$.

8) The resulting precipitates having high molar ratios (divalent cation :ATMP) offered the high initial rates of dissolution because their solubility limit as a driving force tended to be high as well.

9) Magnesium found in the resulting precipitates came from the formation of Mg-ATMP precipitates participating with Ca-ATMP precipitates or, in the other words, Mg-ATMP precipitates can be able to co-precipitate along with Ca-ATMP precipitates under the same conditions. This attribution was directly supported by the results from batch dissolution whereas the initial rates of Mg-ATMP precipitates were approximately two times higher than those of Ca-ATMP precipitates.

5.2 Recommendations

The extremely important goal for precipitation squeeze treatment is to acquire the maximum squeeze lifetime, therefore in order to know which resulting precipitates can offer the maximum squeeze lifetime, micromodel experiment should be performed. In addition, the micromodel unit simulated as porous media in oil reservoir also demonstrates the release mechanism of the resulting precipitates via a stereo-zoom microscrope and continuously records all events by using a super VHS video recorder.

To obtain more reliable results, the actual conditions such as the temperature, varying solution pH and other divalent cations should be concerned because these factors can affect the formation and the properties of precipitates.