

REFERENCES

- Browning, F.H., and Fogler, H.S. (1993). Precipitation and dissolution of Calcium-phosphonate for the enhancement of squeeze lifetime. paper SPE 25164 presented at the SPE International Symposium on Oilfield Chemistry, New Orleans, LA, 137-147.
- Browning, F.H., and Fogler, H.S. (1995). Effect of synthesis parameter on properties of calcium phosphonate precipitates. Langmuir, 11, 4143-4152.
- Browning, F.H., and Fogler, H.S. (1996). Effect of precipitates conditions on the Formation of calcium-HEDP precipitates. Langmuir, 12, 5231-5238.
- Carlberg, B.L. (1987). Scale inhibitor precipitation squeeze for non-carbonate Reservoirs. paper SPE 17008 presented at the Production Technology Symposium, Lubbock, TX.
- Gill, J.S., Anderson, C.D., and Varsanik, R.G. (1985). Mechanism of scale inhibition by phosphonates. paper IWC-83-4 presented at the International Water Conference, 26.
- Howard, B.B., Fred, W.G., and Mohamed, M. (1987). Petroleum engineering handbook. Texas: Society of Petroleum Engineers.
- King, G.E., and Warden, S.L. (1989). Introductory work in scale inhibitor Squeeze performance, core tests and field results. paper SPE 18485 presented at the SPE International Symposium in Oilfield Chemistry, Houston, Texas.
- Kan, A.T., Yan, L., Bedient, P.B., Oddo, J.E., and Tomson, M.B. (1991) Determination of low concentration of phosphonate in brines. paper SPE 21006 presented at the SPE International Symposium on Oilfield Chemistry, Anaheim, California.

- Lewis, A.L., and Raju, K.U. (1992). Some important chemistry of amino tri methylene phosphonic acid, The International Conference on Chemistry in Industry, proceedings part 1, 533-547.
- Liwsrisakul, J. (1999). Precipitation, transformation and re-dissolution of calcium scale inhibitor (HEDP) in porous media. Master Thesis in the Petrochemical Technology, the Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Myers, K.O., Skillman, H.L., and Herring, G.D. (1985). Control of formation Damage at Prudhoe Bay, Alaska, by inhibitor squeeze treatment. Journal of Petroleum Technology, 1019-1034.
- Martell, A.E., and Calvin, M. (1956). Chemistry of the metal chelate compounds. New Jersey: PrenticeHall.
- Monsanto Technical Bulletin (1986). Dequest 2060 Phosphonate. Publication WT-8601.
- Nancollas, G.H. (1987). The inhibition of scale formation involving calcium and barium salts. paper no. 372, presented at NACE Corrosion '87 in San Francisco, CA
- Oddo, J.E., and Tomson, M.B. (1990) The solubility and stoichiometry of Calcium-DTPMP at 70 C in brine solutions. Applied Geochemistry, 5, 527-532.
- Plummer, F.B. (1945). Treatment of oil wells to remove carbonate scales. Oil and Gas Journal, 44(1).
- Perrin, D.D. (1974). Buffer for pH and metal ion control. Boyd Dempsey: Chapman and Hall Ltd.
- Przybylinski, J.L. (1989). Adsorption and desorption characteristics of mineral Scale inhibitors as related to the design of squeeze treatments. paper SPE 18486 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 8-10.

- Raju, K.U. (1998). CaCO₃ scaling tendency can differ over seawater flood Life. Oil and Gas Journal, 55-56.
- Rerkpattanapipat, P. (1996). Precipitation and dissolution of calcium-phosphonate on inhibition of scale formation in porous media. Master Thesis in the Petrochemical Technology, the Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Shuler, P.J. (1991). Method for prolonging the useful life of scale inhibitors Injected within a formation. U.S. Patent No 5038861.
- Schalge, A.L. (1990). Marathon Oil Company, personal communication.
- Suwannamek, I. (1998). Dissolution of scale inhibitor (DTPMPA) in porous media. Master Thesis in the Petrochemical Technology, the Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Sorbie, K.S., Yuan, M.D., Chen, P., Todd, A.C., and Wat, R.M.S. (1993). The effect of pH on the adsorption and transport of phosphonate scale Inhibitor through porous media. Paper SPE 25165 presented at the Oilfield Chemistry, New Orleans.
- Vetter, O.J. (1972). An evaluation of scale inhibitors. Journal of Petroleum Technology, 997.
- Willhite, G.P. (1986). Waterflooding. Texas: Society of Petroleum Engineers.
- Wattana, P. (1997). Dissolution kinetics of scale inhibitors in the presence of high concentration of calcium. Master Thesis in the Petrochemical Technology, the Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

- Wattanasakwiboon, W. (2000). Effect of precipitating conditions on the formation of magnesium-HEDP precipitates. Master Thesis in the Petrochemical Technology, the Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Yuan, M.D., Sorbie, K.S., and Todd, A.C. (1993). The modeling of Adsorption and precipitation scale inhibitors squeeze treatments in north sea field. paper SPE 25163 presented at the SPE International Symposium on Oilfield Chemistry, New Orleans, 121-136.

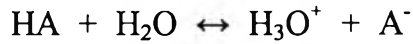
APPENDIX A

Calculation Method for the Deprotonation Curves for ATMP

1. Equilibrium acid constant

The equilibrium acid constant is defined in terms of the activity of product species divided by reactant species as shown below

For example;



The equilibrium acid constant is written as

$$Ka = \frac{(H_3O^+)(A^-)}{(HA)} \quad (1)$$

where () denote the activities of the hydrated species

Rearrange eq(1),

$$(H_3O^+) = \frac{Ka(HA)}{(A^-)} \quad (2)$$

Taking the logarithms both sides of eq (2),

$$-\log(H_3O^+) = -\log \left[Ka \frac{(HA)}{(A^-)} \right] \quad (3)$$

Rearrange eq(3),

$$-\log(H_3O^+) = - \left[\log Ka - \log \frac{(A^-)}{(HA)} \right] \quad (4)$$

where $pH = -\log(H_3O^+)$ and $pKa = -\log Ka$

Eq(4) becomes,

$$pH = pKa + \log \frac{(A^-)}{(HA)} \quad (5)$$

or

$$pH = pKa + \log \frac{(\text{basic species})}{(\text{acidic species})} \quad (6)$$

2. Activity

The activity is defined as,

$$a_i = C_i f_i \quad (7)$$

where

C_i = concentration (M)

f_i = activity coefficient

Substituting eq(7) into eq(1),

$$Ka = \frac{(C_{H_3O^+} f_{H_3O^+})(C_{A^-} f_{A^-})}{(C_{HA} f_{HA})} \quad (8)$$

Rearrange,

$$Ka = \frac{C_{H_3O^+} C_{A^-}}{C_{HA}} \cdot \frac{f_{H_3O^+} f_{A^-}}{f_{HA}} \quad (9)$$

$$\frac{C_{H_3O^+} C_{A^-}}{C_{HA}} = Ka \frac{f_{HA}}{f_{H_3O^+} f_{A^-}} \quad (10)$$

$$\text{where } Ka' = \frac{C_{H_3O^+} C_{A^-}}{C_{HA}}$$

Eq10 becomes,

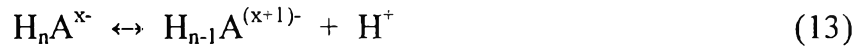
$$Ka' = Ka \frac{f_{HA}}{f_{H_3O^+} f_{A^-}} = F(T, f_i) \quad (11)$$

In order to be comfortable, eq 6 is used in terms of molar concentration unit (M), hence the eq 6 is expressed as

$$pH = pKa' + \log \frac{[\text{basic species}]}{[\text{acidic species}]} \quad (12)$$

where [] represents the molar concentration unit

In general, the equilibrium reaction of acid is shown as



From eq 12,

$$pH = pKa + \log \frac{[H_{n-1} A^{(x+1)-}]}{[H_n A^{x-}]} \quad (14)$$

Eq 10 demonstrates that Ka' is a function of temperature (T) and activity coefficient (f_i), however the activity coefficient is also depend upon the ionic strength (I) as shown in Debye-Huckel equation.

The Debye-Huckel equation for dilute solution is written as;

$$-\log f_i = \frac{AZ^2 I^{0.5}}{(1 + I^{0.5})} - 0.1Z^2 I \quad (\text{only dilute solution}) \quad (15)$$

where

f_i = activity coefficient [-]

I = ionic strength [M]

A = a constant which depends on the temperature

(at 25°C, $A = 0.512$)

Z = charge

From eq 15, eq 14 becomes;

$$pH = pKa - \frac{(2x+1)BI^{1/2}}{(1 + I^{1/2})} + 0.1(2x+1)I + \log \frac{[H_{n-1} A^{(x+1)-}]}{[H_n A^{x-}]} \quad (16)$$

$$pKa' = pKa - \frac{(2x+1)BI^{1/2}}{(1+I^{1/2})} + 0.1(2x+1)I \quad (17)$$

3. Calculation of the fraction of ATMP species

The Amino trimethylene phosphonic acid (ATMP) is a polyprotic acid which dissociates in several steps expressed in terms of six of equilibrium acid constants as shown below;

$$Ka_1 = \frac{[ATMP^-][H^+]}{[ATMP]} \quad (18)$$

$$Ka_2 = \frac{[ATMP^{2-}][H^+]}{[ATMP^-]} \quad (19)$$

$$Ka_3 = \frac{[ATMP^{3-}][H^+]}{[ATMP^{2-}]} \quad (20)$$

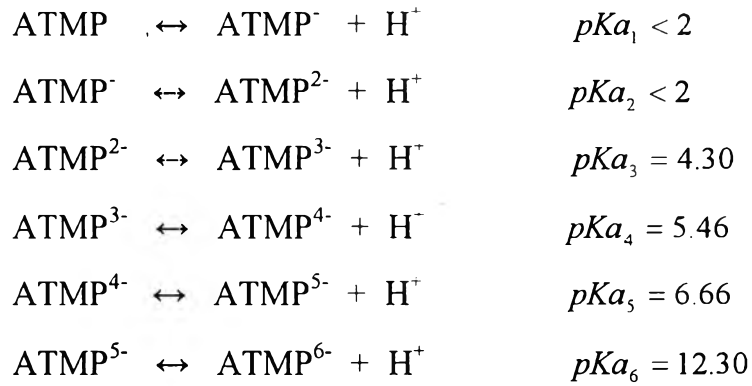
$$Ka_3 = \frac{[ATMP^{3-}][H^+]}{[ATMP^{2-}]} \quad (21)$$

$$Ka_4 = \frac{[ATMP^{4-}][H^+]}{[ATMP^{3-}]} \quad (22)$$

$$Ka_5 = \frac{[ATMP^{5-}][H^+]}{[ATMP^{4-}]} \quad (23)$$

$$Ka_6 = \frac{[ATMP^{6-}][H^+]}{[ATMP^{5-}]} \quad (24)$$

The following values are the equilibrium acid constant of ATMP at 25 C



The total ATMP concentration is the sum of above species

$$\text{ATMP}_{\text{Total}} = [\text{ATMP}^{6-}] + [\text{ATMP}^{5-}] + [\text{ATMP}^{4-}] + \dots + [\text{ATMP}^{1-}] + [\text{ATMP}] \quad (25)$$

From the equilibrium reaction indicating the several deprotonation steps of ATMP, the concentration of each deprotonated species can be expressed as;

$$[\text{ATMP}] = \frac{[\text{ATMP}^-][\text{H}^+]}{K_{a_1}} \quad (26)$$

$$[\text{ATMP}^-] = \frac{[\text{ATMP}^{2-}][\text{H}^+]}{K_{a_2}} \quad (27)$$

$$[\text{ATMP}^{2-}] = \frac{[\text{ATMP}^{3-}][\text{H}^+]}{K_{a_3}} \quad (28)$$

$$[\text{ATMP}^{3-}] = \frac{[\text{ATMP}^{4-}][\text{H}^+]}{K_{a_4}} \quad (29)$$

$$[\text{ATMP}^{4-}] = \frac{[\text{ATMP}^{5-}][\text{H}^+]}{K_{a_5}} \quad (30)$$

$$[\text{ATMP}^{5-}] = \frac{[\text{ATMP}^{6-}][\text{H}^+]}{K_{a_6}} \quad (31)$$

From eq 16 and 17, all deprotonated species above can be written in terms of pH and pKa' as shown below;

$$[ATMP] = [ATMP^{1-}] 10^{pKa_1' - pH} \quad (32)$$

$$[ATMP^{1-}] = [ATMP^{2-}] 10^{pKa_2' - pH} \quad (33)$$

$$[ATMP^{2-}] = [ATMP^{3-}] 10^{pKa_3' - pH} \quad (34)$$

$$[ATMP^{3-}] = [ATMP^{4-}] 10^{pKa_4' - pH} \quad (35)$$

$$[ATMP^{4-}] = [ATMP^{5-}] 10^{pKa_5' - pH} \quad (36)$$

$$[ATMP^{5-}] = [ATMP^{6-}] 10^{pKa_6' - pH} \quad (37)$$

where

$$pKa_1' = pK_1 - \frac{BI^{1/2}}{(1+I^{1/2})} + 0.1I - pH \quad (38)$$

$$pKa_2' = pK_2 - \frac{3BI^{1/2}}{(1+I^{1/2})} + 0.3I - pH \quad (39)$$

$$pKa_3' = pK_3 - \frac{5BI^{1/2}}{(1+I^{1/2})} + 0.5I - pH \quad (40)$$

$$pKa_4' = pK_4 - \frac{7BI^{1/2}}{(1+I^{1/2})} + 0.7I - pH \quad (41)$$

$$pKa_5' = pK_5 - \frac{9BI^{1/2}}{(1+I^{1/2})} + 0.9I - pH \quad (42)$$

$$pKa_6' = pK_6 - \frac{11BI^{1/2}}{(1+I^{1/2})} + 1.1I - pH \quad (43)$$

Substituting eq 32-43 in eq 25;

$$ATMP_{Total} = [ATMP^-] 10^{pKa_1'} + [ATMP^{2-}] 10^{pKa_2'} + [ATMP^{3-}] 10^{pKa_3'} + \dots + [ATMP^{6-}] \quad (44)$$

Rearrange eq 44;

$$ATMP_{Total} = [ATMP^{6-}] (1 + 10^{pKa_6} + 10^{pKa_6 + pKa_5} + \dots + 10^{pKa_6 + pKa_5 + pKa_4 + pKa_3 + pKa_2 + pKa_1}) \quad (45)$$

$$\text{where } Z = (1 + 10^{pKa_6} + 10^{pKa_6 + pKa_5} + \dots + 10^{pKa_6 + pKa_5 + pKa_4 + pKa_3 + pKa_2 + pKa_1}) \quad (46)$$

Therefore,

$$[ATMP^{6-}] = \frac{ATMP_{Total}}{Z} \quad (47)$$

$$\text{Fraction of } [ATMP^{6-}] \text{ species} = \frac{[ATMP^{6-}]}{ATMP_{Total}} = \frac{1}{Z} \quad (48)$$

In the same manner for every deprotonated species;

$$\text{Fraction of } [ATMP^{5-}] \text{ species} = \frac{[10^{pKa_6}]}{Z} \quad (49)$$

$$\text{Fraction of } [ATMP^{4-}] \text{ species} = \frac{[10^{pKa_6 + pKa_5}]}{Z} \quad (50)$$

$$\text{Fraction of } [ATMP^{3-}] \text{ species} = \frac{[10^{pKa_6 + pKa_5 + pKa_4}]}{Z} \quad (51)$$

$$\text{Fraction of } [ATMP^{2-}] \text{ species} = \frac{[10^{pKa_6 + pKa_5 + pKa_4 + pKa_3}]}{Z} \quad (52)$$

$$\text{Fraction of } [ATMP^{-}] \text{ species} = \frac{[10^{pKa_6 + pKa_5 + pKa_4 + pKa_3 + pKa_2}]}{Z} \quad (53)$$

$$\text{Fraction of } [ATMP] \text{ species} = \frac{[10^{pKa_6 + pKa_5 + pKa_4 + pKa_3 + pKa_2 + pKa_1}]}{Z} \quad (54)$$

Substituting the values of $pKa_1, pKa_2, pKa_3, \dots, pKa_6$, the fraction of each deprotonated species of ATMP is obtained.

APPENDIX B**1 Dissolution of 1:1 Ca-ATMP Precipitate in DI Water.****Experimental Conditions:**

Volume of DI water used = 200 ml

Initial solution pH = 5.5

Temperature = room temperature

Rotating Disk Speed = 1000 rpm

Time (min)	Conc. of Ca (M) I	Conc. of Ca (M) II	Conc. of Ca (M) Avg
1	1.5107x10 ⁻⁶	1.2392x10 ⁻⁶	1.3750x10 ⁻⁶
2	3.3333x10 ⁻⁶	2.8123x10 ⁻⁶	3.0728x10 ⁻⁶
3	4.6300x10 ⁻⁶	5.0107x10 ⁻⁶	4.8203x10 ⁻⁶
4	6.5541x10 ⁻⁶	6.2356x10 ⁻⁶	6.3949x10 ⁻⁶

2 Dissolution of 2:1 Ca-ATMP Precipitate in DI water

Experimental Conditions:

Volume of DI water used = 200 ml

Initial solution pH = 5.5

Temperature = room temperature

Rotating Disk Speed = 1000 rpm

Time (min)	Conc. of Ca (M) I	Conc. of Ca (M) II	Conc. of Ca (M) Avg
1	5.4644×10^{-7}	8.1529×10^{-7}	6.8086×10^{-7}
2	1.4509×10^{-6}	1.7702×10^{-6}	1.6106×10^{-6}
3	2.1329×10^{-6}	2.5166×10^{-6}	2.3247×10^{-6}
4	3.2946×10^{-6}	3.9359×10^{-6}	3.6153×10^{-6}

3 Dissolution of 3:1 Ca-ATMP Precipitate in DI water

Experimental Conditions:

Volume of DI water used = 200 ml

Initial solution pH = 5.5

Temperature = room temperature

Rotating Disk Speed = 1000 rpm

Time (min)	Conc. of Ca (M) I	Conc. of Ca (M) II	Conc. of Ca (M) Avg
1	4.5656x10 ⁻⁷	7.0715x10 ⁻⁷	5.8185x10 ⁻⁷
2	1.2619x10 ⁻⁶	1.4650x10 ⁻⁶	1.3635x10 ⁻⁶
3	1.7478x10 ⁻⁶	2.0285x10 ⁻⁶	1.8881x10 ⁻⁶
4	2.5197x10 ⁻⁶	2.7549x10 ⁻⁶	2.6373x10 ⁻⁶

APPENDIX C**1 Dissolution of 2:1 Mg-ATMP Precipitate in DI Water.****Experimental Conditions:**

Volume of DI water used = 200 ml

Initial solution pH = 5.5

Temperature = room temperature

Rotating Disk Speed = 1000 rpm

Time (min)	Conc. of Mg (M) I	Conc. of Mg (M) II	Conc. of Mg (M) Avg
1	1.0018x10 ⁻⁶	1.5157x10 ⁻⁶	1.2588x10 ⁻⁶
2	2.0321x10 ⁻⁶	3.2178x10 ⁻⁶	2.6250x10 ⁻⁶
3	4.7375x10 ⁻⁶	5.3137x10 ⁻⁶	5.0256x10 ⁻⁶
4	5.7889x10 ⁻⁶	6.6081x10 ⁻⁶	6.1985x10 ⁻⁶
5	7.6956x10 ⁻⁶	9.1364x10 ⁻⁶	8.4160x10 ⁻⁶

2 Dissolution of 3:1 Mg-ATMP Precipitate in DI Water.

Experimental Conditions:

Volume of DI water used = 200 ml

Initial solution pH = 5.5

Temperature = room temperature

Rotating Disk Speed = 1000 rpm

Time (min)	Conc. of Mg (M) I	Conc. of Mg (M) II	Conc. of Mg (M) Avg
1	8.0142×10^{-7}	1.0018×10^{-6}	9.0160×10^{-7}
2	2.0532×10^{-6}	2.3709×10^{-6}	2.2121×10^{-6}
3	3.8065×10^{-6}	4.9247×10^{-6}	4.3656×10^{-6}
4	5.4407×10^{-6}	6.3739×10^{-6}	5.9073×10^{-6}
5	6.3094×10^{-6}	7.1674×10^{-6}	6.7384×10^{-6}

APPENDIX D

- 1 Dissolution of the Precipitate having Total Molar Ratio of 2:1 and Total Ca/Mg Molar Ratio in the precipitate of 1.35 in DI Water.

Experimental Conditions:

Volume of DI water used = 200 ml

Initial solution pH = 5.5

Temperature = room temperature

Rotating Disk Speed = 1000 rpm

Time (min)	Conc. of Ca (M)	Conc. of Ca (M)	Conc. of Mg (M)	Conc. of Mg (M)
	I	II	I	II
5	7.6260×10^{-7}	3.2342×10^{-7}	1.2736×10^{-6}	8.0921×10^{-7}
10	1.6074×10^{-6}	1.1868×10^{-6}	3.0414×10^{-6}	2.3124×10^{-6}
15	2.5534×10^{-6}	1.9679×10^{-6}	4.6591×10^{-6}	3.7029×10^{-6}
20	3.2347×10^{-6}	2.6429×10^{-6}	6.1137×10^{-6}	5.1562×10^{-6}

2 Dissolution of the Precipitate having Total Molar Ratio of 3:1 and Total Ca/Mg Molar Ratio in the precipitate of 1.21 in DI Water.

Experimental Conditions:

Volume of DI water used = 200 ml

Initial solution pH = 5.5

Temperature = room temperature

Rotating Disk Speed = 1000 rpm

Time (min)	Conc. of Ca (M)	Conc. of Ca (M)	Conc. of Mg (M)	Conc. of Mg (M)
	I	II	I	II
5	2.9549x10 ⁻⁷	4.3611x10 ⁻⁷	1.3150x10 ⁻⁶	6.0655x10 ⁻⁷
10	1.3618x10 ⁻⁶	8.1418x10 ⁻⁷	2.3225x10 ⁻⁶	1.6668x10 ⁻⁶
15	1.8793x10 ⁻⁶	1.5877x10 ⁻⁶	3.7088x10 ⁻⁶	3.1771x10 ⁻⁶
20	2.4219x10 ⁻⁶	2.0418x10 ⁻⁶	4.8412x10 ⁻⁶	4.2667x10 ⁻⁶

CURRICULUM VITAE

Name: Mongkol Bualuang

Date of Birth: 5 May 1976

Nationality: Thai

University Education:

1995-1998 Bachelor Degree of Engineering in Chemical Engineering,
King Mongkut's University of Technology Thonburi,
Bangkok, Thailand.