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APPENDICES

Appendix A Typical properties of Aminotri(methylene phosphonic acid)

Structure.

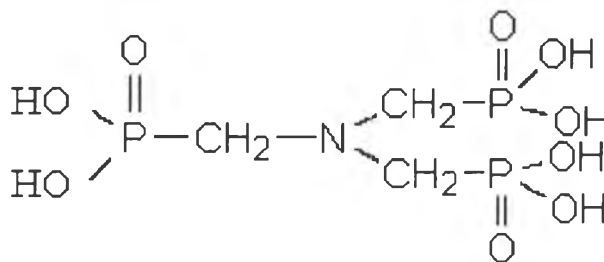


Figure A Molecular structure of ATMP.

Physical properties

Synonym	Nitrilotrimethylene triphosphonic acid
Abbreviation	ATMPA, ATMP
Molecular formula	$C_3H_{12}N_3O_9P_3$
Molecular weight	299.0
Molar volume, cm^3	142.7
Appearance	Clear water, white to pale yellow aqueous solution
Active content	50% (as acid)
Specific gravity, 20/20°C	1.33
pH, 1% solution at 25°C	< 2
Freezing point, °C	-15
Boiling point, °C	> 105
Chloride as Cl, %	< 1
Iron (Fe), ppm	< 35

Functional properties

$CaCO_3$ inhibition	Excellent
$CaSO_4$ inhibition	Good
Calcium compatibility	Good
Iron control	Yes
Sequestration	Good
Steel corrosion inhibition (formulated)	Excellent

* Above referred specifications are belong to Monsanto

Appendix B Calculation method for deprotonation and metal complexation of ATMP.

In order to calculate and predict the effects of solution composition on the squeeze treatment performance, it is necessary to understand the acid/base and complex solution chemistry as a function of pH, temperature, and ionic strength. The proton and calcium association scheme depicted in Figure B will be used to represent the solution chemistry of ATMP in the presence of calcium. The deviations will be written in terms of an arbitrary phosphonic acid with n-ionizable protons, $H_n\text{Phn}$.

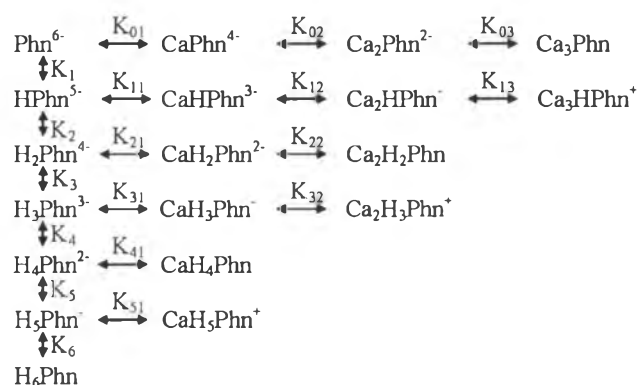


Figure B A representation of all ATMP and calcium complexes considered in the present model. Stepwise association constants are to the right or just above the respective arrows.

The first association constant is defined by the following reaction and equation



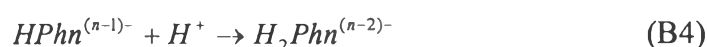
$$K_1 = \frac{(\text{HPhn}^{(n-1)-})}{\{\text{H}^+\} \{\text{Phn}^{n-}\}} \quad (\text{B2})$$

where parentheses refer to concentration, $\{\text{H}^+\}$ refers to activity and is given by $\{\text{H}^+\} = 10^{-\text{pH}}$, and n represents the value of the charge on the completely deprotonated phosphonate molecule (for ATMP, n= 6). The concentration of

the protonated species, ($HPhn^{(n-1)-}$), can be expressed in terms of K_1 , the free phosphonate concentration, measured pH

$$(HPhn^{(n-1)-}) = K_1 \{H^+\} (Phn^{n-}) \quad (B3)$$

Similarly, the second association reaction and constant are given by

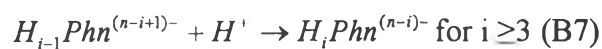


$$K_2 = \frac{(H_2Phn^{(n-2)-})}{\{H^+\} \{HPhn^{(n-1)-}\}} \quad (B5)$$

By substituting Equation (B3) into Equation(B5), the concentration of the species, ($H_2Phn^{(n-2)-}$), can be expressed in terms of already measured equilibrium constants, the free phosphonate concentration, and pH

$$(H_2Phn^{(n-2)-}) = K_1 K_2 \{H^+\}^2 (Phn^{n-}) \quad (B6)$$

The remaining proton association reactions and constants can be represented by the following equation:



$$K_i = \frac{(H_iPhn^{(n-i)-})}{\{H^+\} \{H_{i-1}Phn^{(n-i+1)-}\}} \quad (B8)$$

By continuing the substitution, as in Equation (B6), an arbitrary phosphonate species, ($H_iPhn^{(n-i)-}$), can be expressed in terms of equilibrium constants, free phosphonate concentration, and pH

$$(H_i Phn^{(n-i)-}) = K_1 K_2 K_3 \dots K_i \{H^+\}^i (Phn^{n-}) \quad \text{for } i \geq 3 \quad (\text{B9})$$

To simplify terms, the “beta” or cumulative formation constant notation will be used and charges will be dropped:

$$\beta_1 = K_1 \quad (\text{B10})$$

$$\beta_2 = K_1 K_2 \quad (\text{B11})$$

$$\text{and} \quad \beta_i = K_1 K_2 K_3 \dots K_i \quad \text{for } i \geq 3 \quad (\text{B12})$$

A model can now be proposed to calculate the values of the K_i 's, assuming the primary difference between successive equilibrium constants is a consequence of decreasing charge. The following model is proposed to calculate the values of K_i 's for the proton association equilibria.

$$\log K_i = a_H + b_H / |q_{i-1}| \quad (\text{B13})$$

where a_H and b_H are constants which depend on ionic strength and temperature to be determined from the following equations and $|q_{i-1}|$ represents the absolute value of charge on the $(i-1)^{\text{th}}$ species.

$$a_H = 2.296 - 0.567\sqrt{I(M)} + 0.184 \cdot I(M) - \frac{314}{T(K)} \quad (\text{B14})$$

$$b_H = 1.439 - 0.160\sqrt{I(M)} + 0.0255 \cdot I(M) - \frac{54.3}{T(K)} \quad (\text{B15})$$

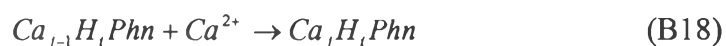
The mass balance for the total phosphonate, C_{phn} , is given by

$$C_{phn} = (Phn) + \sum_{i=1}^{i=n} (H_i Phn) \quad (\text{B16})$$

Substituting Equation (B9) into Equation (B16) and factoring out the concentration of free phosphonate, (Phn), yields:

$$(Phn) = \frac{C_{Phn}}{1 + \sum_{i=1}^{i=n} \beta_i \{H^+\}^i} \quad (B17)$$

The procedure for calculating the stability constants of the calcium-ATMP complexes using an electrostatic model is similar to that outlined above for the proton equilibria. Again, the speciation scheme depicted in Figure B will be used. The general reaction and equilibrium constant for the formation of a calcium-ATMP complex are as follows:



$$K_{ij} = \frac{(Ca_jH_iPhn)}{\{Ca^{2+}\}(Ca_{j-1}H_iPhn)} \quad (B19)$$

By repeated substitution, the concentration of (Ca_jH_iPhn) can be expressed as

$$(Ca_jH_iPhn) = \beta_i K_{i1} K_{i2} \dots K_{ij} (Ca^{2+})^j \{H^+\}^i (Phn) \quad (B20)$$

Again, the formation constants, K_{ij} , can be modeled with an equation similar to Equation (B13), which assumes that the stability constant is proportional to the charge on the species with one less calcium ion

$$\log K_{ij} = a_{Ca} + b_{Ca} / q_{2(j-1)+i} \quad (B21)$$

The value of a_{Ca} determined from statistic analysis was not distinguishable from zero. Therefore, it was set to zero and the final model used was

$$\log K_{ij} = b_{Ca} / q_{2(j-1)+i} \quad (B22)$$

where b_{Ca} is constants which depend on ionic strength and temperature to be determined from the following equation

$$b_{Ca} = 1.569 - 0.606\sqrt{I(M)} + 0.201 \cdot I(M) - \frac{206}{T(K)} \quad (B23)$$

The cumulative formation for the metal complexes can be written in terms of the individual proton association constants and the individual calcium-phosphate stability constants:

$$\beta_{ij} = K_1 K_2 \dots K_i K_{i1} K_{i2} \dots K_{ij} = \beta_i K_{i1} K_{i2} \dots K_{ij} \quad (B24)$$

The following equations present final forms of equations needed to calculate the concentration of free calcium, free phosphonate, and calcium-phosphonate species. The algebraic procedure is slightly more involved because it required the simultaneous solution of two mass balance equations, one for phosphonate (C_{Phn}) and one for total calcium (C_{Ca}). The two mass balance equations are

$$C_{Ca} = (Phn) + (HPhn) + \sum_{i=2}^n \sum_{j=0}^{(n-i)/2} (Ca_j H_i Phn) \quad (B25)$$

$$C_{Ca} = (Ca) + \sum_{i=2}^n \sum_{j=0}^{(n-i)/2} (j)(Ca_j H_i Phn) \quad (B26)$$

By substitution of Equation (B6) and Equation (B20) into Equation (B25) and factoring out (Phn) the following equation for free phosphate can be derived in terms of pH, free calcium, and β_{ij} 's

$$(Phn) = \frac{C_{Phn}}{1 + K_1\{H^+\} + \sum_{i=1}^{i=n} \sum_{j=0}^{(n-i)/2} \beta_{ij}(Ca)^j \{H^+\}^i} \quad (B27)$$

The effect of complex formation on the concentration of free calcium can be determined by substituting Equation (B20) into Equation (B26) and using Equation (B27) to eliminate (Phn)

$$C_{Ca} = (Ca) + \frac{\sum_{i=2}^n \sum_{j=0}^{(n-i)/2} (j)\beta_{ij}(Ca)^j \{H^+\}^i C_{Phn}}{1 + K_1\{H^+\} + \sum_{i=1}^{i=n} \sum_{j=0}^{(n-i)/2} \beta_{ij}(Ca)^j \{H^+\}^i} \quad (B28)$$

For any specific solution of known pH, total calcium and phosphonate concentrations, Equation (B28) is a polynomial in one unknown, free calcium concentration (Ca) , which can be solved by various iteration procedures. Once (Ca) is calculated, it can be substituted into Equation (B27) to calculate (Phn) . Then, the concentration of any species can be calculated using Equation (B9) and Equation (B20).

Appendix C Experimental data.

No.	[ATMP] initial (mol/l)	Salt (mol/l)	pH	[ATMP] eq (mol/l)	Initial		final		S	tind (s)
					[Ca ²⁺]	[ATMP ²⁻]	[Ca ²⁺]	[ATMP ²⁻]		
1	0.113	-	1.5	0.028	0.104	4.30E-32	0.027	7.57E-34	219.60	35
2	0.090	-	1.5	0.020	0.085	2.08E-32	0.020	3.60E-34	247.52	35
3	0.075	-	1.5	0.020	0.071	1.18E-32	0.019	3.44E-34	125.78	65
4	0.049	-	1.5	0.016	0.047	3.35E-33	0.016	2.30E-34	42.51	110
5	0.045	-	1.5	0.018	0.044	2.68E-33	0.016	2.30E-34	31.57	195
6	0.039	-	1.5	0.019	0.039	1.88E-33	0.016	2.30E-34	19.64	475
7	0.038	-	1.5	0.013	0.037	1.65E-33	0.016	2.30E-34	16.27	592
8	0.033	-	1.5	0.013	0.033	1.22E-33	0.016	2.30E-34	10.77	737
9	0.030	-	1.5	0.016	0.029	9.37E-34	0.016	2.30E-34	7.42	1837
10	0.028	-	1.5	0.020	0.028	8.00E-34	0.016	2.30E-34	5.95	2097
11	0.090	LiCl 0.05 M	1.5	0.022	0.085	3.07E-32	0.022	1.04E-33	115.01	25
12	0.075	LiCl 0.05 M	1.5	0.023	0.071	1.82E-32	0.022	1.10E-33	52.37	55
13	0.064	LiCl 0.05 M	1.5	0.017	0.061	1.17E-32	0.017	6.39E-34	66.37	85
14	0.049	LiCl 0.05 M	1.5	0.015	0.047	5.87E-33	0.015	5.14E-34	36.24	165
15	0.045	LiCl 0.05 M	1.5	0.015	0.044	4.83E-33	0.015	4.96E-34	29.14	255
16	0.042	LiCl 0.05 M	1.5	0.016	0.041	4.18E-33	0.016	5.81E-34	18.61	376
17	0.039	LiCl 0.05 M	1.5	0.013	0.038	3.52E-33	0.013	4.20E-34	24.39	345
18	0.035	LiCl 0.05 M	1.5	0.016	0.034	2.76E-33	0.016	5.74E-34	10.48	715
19	0.090	NaCl 0.05M	1.5	0.019	0.085	3.07E-32	0.019	8.05E-34	169.73	35
20	0.075	NaCl 0.05M	1.5	0.018	0.071	1.82E-32	0.018	7.23E-34	99.89	65
21	0.064	NaCl 0.05M	1.5	0.016	0.061	1.17E-32	0.016	5.81E-34	77.09	75
22	0.049	NaCl 0.05M	1.5	0.013	0.047	5.87E-33	0.013	4.25E-34	48.99	185

No.	[ATMP] initial (mol/l)	Salt (mol/l)	pH	[ATMP] eq (mol/l)	Initial		final		S	tind (s)
					[Ca ²⁺]	[ATMP ²⁻]	[Ca ²⁺]	[ATMP ²⁻]		
23	0.045	NaCl 0.05M	1.5	0.013	0.044	4.83E-33	0.013	4.09E-34	39.60	165
24	0.042	NaCl 0.05M	1.5	0.013	0.041	4.18E-33	0.013	3.99E-34	33.72	463
25	0.034	NaCl 0.05M	1.5	0.012	0.033	2.49E-33	0.011	3.32E-34	21.67	1355
26	0.030	NaCl 0.05M	1.5	0.011	0.029	1.93E-33	0.011	3.23E-34	15.66	2460
27	0.090	KCl 0.05 M	1.5	0.021	0.085	3.07E-32	0.020	9.09E-34	140.95	35
28	0.075	KCl 0.05 M	1.5	0.019	0.071	1.82E-32	0.019	7.67E-34	91.18	45
29	0.064	KCl 0.05 M	1.5	0.017	0.061	1.17E-32	0.017	6.19E-34	69.70	95
30	0.049	KCl 0.05 M	1.5	0.016	0.044	4.83E-33	0.014	4.85E-34	30.22	225
31	0.045	KCl 0.05 M	1.5	0.015	0.047	5.87E-33	0.016	5.81E-34	29.90	395
32	0.042	KCl 0.05 M	1.5	0.014	0.041	4.18E-33	0.014	4.52E-34	27.67	418
33	0.039	KCl 0.05 M	1.5	0.014	0.038	3.52E-33	0.014	4.63E-34	20.89	909
34	0.035	KCl 0.05 M	1.5	0.014	0.034	2.76E-33	0.014	4.52E-34	15.31	1515
35	0.049	-	1.5	0.016	0.047	3.35E-33	0.016	2.30E-34	42.51	90
36	0.049	NaClO.025M	1.5	0.013	0.047	4.49E-33	0.013	2.63E-34	61.56	115
37	0.049	NaClO.050M	1.5	0.013	0.047	5.87E-33	0.013	4.25E-34	48.99	120
38	0.049	NaClO.100M	1.5	0.017	0.047	9.44E-33	0.016	1.23E-33	21.92	130
39	0.049	LiCl 0.025M	1.5	0.010	0.047	4.49E-33	0.010	1.77E-34	114.76	105
40	0.049	LiCl 0.050M	1.5	0.015	0.047	5.87E-33	0.015	5.14E-34	36.24	115
41	0.049	LiCl 0.100M	1.5	0.015	0.047	9.44E-33	0.015	1.08E-33	26.99	115
42	0.049	KCl 0.025 M	1.5	0.014	0.047	4.49E-33	0.013	2.77E-34	56.61	115
43	0.049	KCl 0.050 M	1.5	0.016	0.047	5.87E-33	0.016	5.81E-34	29.90	145
44	0.049	KCl 0.100 M	1.5	0.017	0.047	9.44E-33	0.016	1.22E-33	22.27	170
45	0.039	-	1.5	0.019	0.039	1.88E-33	0.016	2.30E-34	19.64	475
46	0.039	-	4.0	0.016	0.021	4.75E-31	0.016	2.12E-34	3041.37	2220
47	0.039	-	7.0	0.021	0.002	5.01E-35	0.020	3.94E-34	0.01	0

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