Supplementary information

Title: The state of the art in scale inhibitor squeeze treatment

Authors: Amy T Kan *[1], Zhaoyi (Joey) Dai [1], Mason B. Tomson [1]

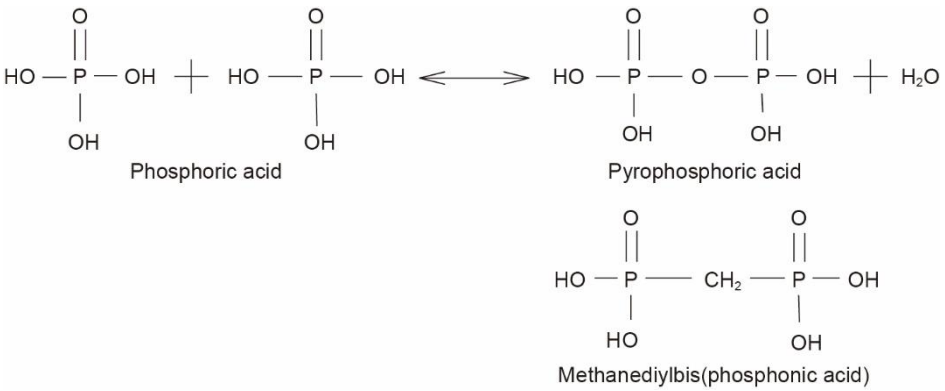
[1] Department of Civil and Environmental Engineering, Rice University, 6100 Main Street, Houston, TX 77005, US

* Corresponding Author: atk@rice.edu

A. Review of advances in related fields of science of phosphonate and phosphate chemistry

Phosphonates are chemically similar to phosphates, both are Pearson Type A hard sphere acids of sp^3 hybridized phosphorous, and as such form electrostatic hard sphere complexes with alkaline earth metal ions (Mg^{2+}, Ca^{2+}, etc.). The Linus Pauling rule of "oxy-acids" (subsequent ionization constants differ by five orders of magnitude) holds for both phosphate and for phosphonates (upon examining H^+ dissociations from each phosphonates moiety, $R{-}PO_3H_2$). Also, phosphonates form insoluble salts with Ca^{2+} and even more insoluble solids with Fe^{2+}, analogous to calcium and iron (II) phosphates. Consequently, insights gained from years of research on phosphates might be expected to inform our understanding of phosphonates, and in fact many parallels have been observed. Calcium phosphates of various forms are the most common source of phosphates for fertilizer and for the skeletal members of all mammals, and therefore it is expected that insights gained from these fields of study might be good guides for phosphonates. Pyrophosphate is reported to inhibit calcite precipitation at 1E-7 M, and below, consistent with a Langmuir adsorption isotherm, but this corresponds to about 0.02 mg/L of pyrophosphate. Adsorption of 1 mg of inhibitor will cover about 1 m^2 of surface area, so this low Langmuir adsorption concentration probably implies adsorption to only the active kink sites in the solid calcite(Tomson et al. 2003).

It is generally proposed that pyrophosphate ($P_2O_7^{4-}$, chemical formulas S1) is the biological inhibitor of e.g. kidney stones, etc. pyrophosphate, ($P_2O_7^{4-}$) is an excellent mineral scale inhibitor, but it undergoes hydrolysis to two phosphate groups. It is pyrophosphate that is added many brands of tooth paste as tarter control. The similar compound, but with the bridging oxygen replaced by a methylene group ($-CH_2-$), was synthesized and found to be an excellent scale inhibitor and resistant to hydrolysis.



Chemical formulas S1

Due to all the chemical similarity of phosphonates to pyrophosphates and phosphates, it is reasonable to expect there to be similarity of the corresponding solid phase formation patterns. Some of the relevant calcium phosphate phases are reviewed below as a backdrop to possibly interpret the calcium phosphonate phases that form during an inhibitor squeeze.

The diagram (Fig. S1) is from oral biology literature and summarizes the relationship of the various phases of calcium phosphate vs. pH (Johnsson and Nancollas 1992). For example, at about 6 pH the order of solubility is as indicated –mono calcium phosphate dehydrate (MCP, in Table S1) is more soluble than dicalcium phosphate dehydrate (DCPD, also called "brushite"), etc.

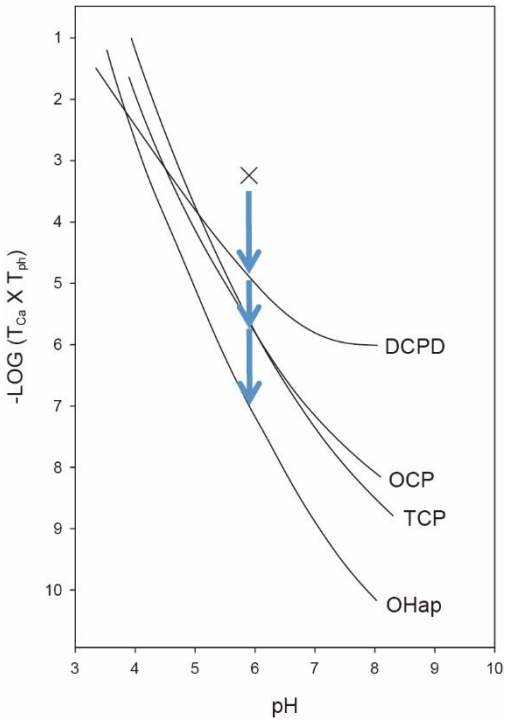


Fig. S1 Solubility isotherms of calcium phosphate phases. The *Y* axis correlates to the ion products of the solid phase constituents. The plots correspond to the conditions in which the ion products are equal to the solubility products (IP=K_{sp}) for a give solid phase. A crystal will experience a net deposition of ions in solutions above and to be right of the curve and will dissolve if the solution is below the curve. These isotherms illustrate the concept that restricting the ionic activity of the enamel fluid can selectively exclude the precipitation of undesirable calcium phosphate solid phases. Reprinted with permission from "The role of brushite and octacalcium phosphate in apatite formation" (Johnsson MS-A, Nancollas GH, Crit Rev Oral Bio Med. 1992;3(1):61-82. CRC Press, Boca Raton, FL)

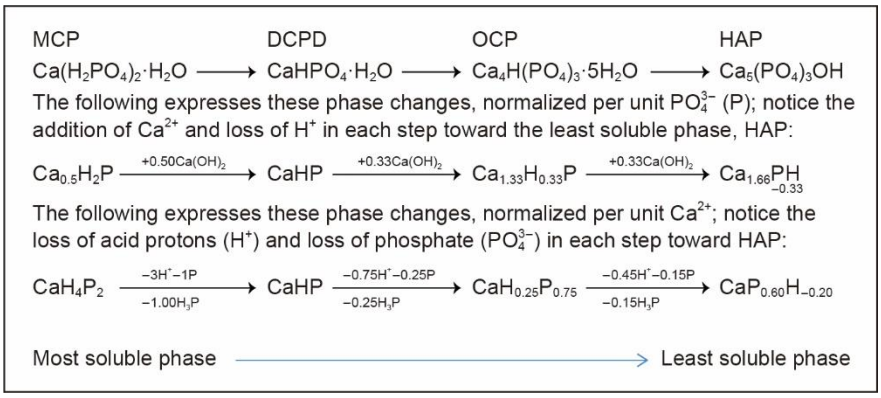
Table S1

Formula	Known as	Ca/PO_4 ratio
$Ca(H_2PO_4)_2 \cdot 2H_2O$	Mono Cal, MCP	0.50
$CaHPO_4 \cdot 2H_2O$	Di Cal, DCPD	1.00
$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	Octa Cal, OCP	1.33
$Ca_5(PO_4)_3OH$	Hydroxy apatite, HAP	1.66

If a solution is initially at the point marked "X" in Fig. S2, i.e. supersaturated with all possible phases shown, it is the most soluble phase that will precipitate first (DCPD, in Fig. S2), not the least soluble phase (HAP, or OHap); this "rule of thumb" is often explained on kinetic basis that the more soluble salts have more waters of hydration and lower interfacial surface tension and therefore are more rapidly nucleated and grow. These phases are similar to each other crystallographically, except for $Ca_3(PO_4)_2$ (TCP), and can be viewed as differing from each other only by the systematic loss of PO_4^{3-} ions, or the acquisition of Ca^{2+} ions and the simultaneous loss of H^+ ions. Progressing from more soluble phase to less soluble phase protons (H^+) are expelled from the solids; at the same time the molar ratio of calcium:phosphate in the solid increases.

These general processes occur in discrete steps, corresponding to the next stable phase in the series, as illustrated in the box, below. In the following chemical formulas (Chemical formulas S2) "P" stands for PO_4^{3-} ion, "-H^+" refers to "OH ", and water molecules are dropped for clarity. These solids share a common crystallographic arrangement of the key phosphate ions in the crystal lattice and therefore the phases can readily convert from one to the next, but once formed often remain metastable for years, or longer. For example, when DCPD forms, as might occur in the above diagram (and does take place in agricultural application of acidic phosphates to calcium rich soils) the DCPD phase often remains metastable, with respect to OCP and HAP, indefinitely. The only known way to precipitate HAP at normal conditions is to prepare a solution just above the HAP curve, but below the OCP solubility and use seed crystals to grow stoichiometric HAP, as was done using a concept called "constant composition," wherein precipitation occurs indefinitely at exactly constant solution concentrations, hence chemical potential (Tomson, Nancollas 1978) .

DCPD and OCP are known precursors of HAP. When a solution is prepared supersaturated only with respect to OCP and HAP and precipitation takes place fast, the only phase formed is OCP, but when the precipitation is slower the solid that forms has a Ca:PO_4 molar ratio of 1.44 Ca:PO_4, which is the exact formula for precipitation of three OCP molecules (1.33 Ca:PO_4) and conversion of one to HAP (1.66 Ca:PO_4), i.e., (2×1.33 + 1×1.66)/3 = 1.44 Ca:PO_4. This material will remain stable indefinitely if left in the solution in which it was precipitated, but if washed with fresh buffered solution, the solid phase will dissolve along the following sequence toward a Ca:PO_4 → 1.66, although slowly. The MCP only precipitates in a highly acidic solution, pH ~ 2, and below, although further study of this phase relationship may inform acidic phosphonate squeezes.



Chemical formulas S2

In the above box the most soluble phase of calcium phosphate that can form does so, i.e., the more "acidic" solid phase with lowest interfacial surface tension nucleates and forms first. Once the more acidic solid phase forms, e.g. DCPD or OCP, the more insoluble basic phases can be developed by either adding calcium ions as $Ca(OH)_2$ and removing phosphate ions, the middle reaction sequence, or equivalently removing both phosphate and hydrogen ions (or the equivalent H_3P) by flushing, or washing the solid –this is what occurs following a calcium phosphonates squeeze, during flow back, and since the brine always has significant calcium very small phosphate (zero phosphonate) it is the loss of phosphoric acid that is more reasonable interpretation –clearly, an area that might be useful for research.

Phosphonate (used in oil and gas squeezes) acid/base, complexation, and solubility chemistry has the potential to be considerably more complex than that of calcium phosphates and it has taken decades to develop a reasonable agreement on the chemistry of Ca-PO_4's. Many of the reactions of phosphonates appear to parallel those of phosphates quite well and in some cases the Ca-Phn's might be more uniform and be better compared with Ca-P_2O_7, in that the third, very basic, proton in H_3PO_4 is not present in phosphonates (as with pyrophosphates), because of the covalent bond formed with phosphorous (R-PO_3H_2). The universality of this analogy might be illustrated with the following table (Table S2) of ionization and stability (of Ca-Phn complexes) constants of phosphoric acid and various mono-phosphonates.

Table S2 pK_1 and pK_2 for mono-phosphonates and for calcium complexes (0.1 M, 25 ºC): Illustrate the common electrostatic effects of phosphoric acid (first row) and several mono-phosphonates

R-PO_3H_2	pK_1	pK_2	pK_3	(pK_2–pK_1)	log10($K_{St}^{Ca\text{-}Phn}$)
HO- (phosphoric)	2.15	7.20		5.05	1.50
CH_3-	2.19	7.55		5.36	1.51
CH_3CH_2-	2.29	7.79		5.50	1.54
$ClCH_2$-	1.04	6.19		5.15	1.46
Cl_2CH_2-	0.70	5.21		4.51	1.26
Cl_3CH_2-	0.80	4.48		3.68	1.25
$BrCH_2$-	1.15	6.24		5.09	1.34
ICH_2-	1.27	6.44		5.14	1.37
$HOCH_2$-	1.70	6.97		5.27	1.68
$H_3N{+}CH_2$-	0.40	5.39	10.05	4.99	1.71
$H_3N{+}CH_2CH_2$-	1.10	6.23	11.02	5.13	1.74
$H_3N{+}CH_2CH_2CH_2$-	1.60	6.89	11.07	5.29	1.68
			av. =	5.20	1.55
			± σ =	0.16	0.14

Most of the data was taken from Smith and Martell, "Critical Stability Constants" Plenum, 1975, New York.

Based upon possible stoichiometry, as illustrated for the phosphates, there could be calcium phosphonate compounds of an enormous variety, at least six (6) possible compounds of NTMP {$N(CH_2PO_3H_2)_3$}, each expected to be more and more insoluble, as m increases, similar to calcium phosphates above:

$$Ca^{2+} + H_6NTMP? \; Ca_{m/2}H_{6-m}NTMP + mH^+ \quad \text{where } m = 1, 2, 3,...6$$

Figure S2 summarizes these observations and is key to understanding the complicated interactions of how phosphonates interact with the calcite in core upon initial injection and reaction to retain $Ca_xH_{6-2x}NTMP$ as a solid/amorphous separated material and as more phosphonate is added more is retained. The critical issue is the mechanism by which desorption from any initial point causes the phase solid phase to desorb quickly toward a common solid product, crystalline $Ca_{2.5}HNTMP_{cr}$.

If the initial solid is below the solubility of the crystalline, $Ca_{2.5}HNTMP_{cr.}$, then it appears to desorb toward another constant level, maybe Ca_3NTMP, but the solubility was too low to characterize well. Apparently, all of the phosphonates, similar to the phosphates, undergo this common type of heterogeneous dissolution (Stumm, Morgan 1996) where in a high solubility initial solid phase undergoes maturation toward a common low solubility phase with an effective lower pH.

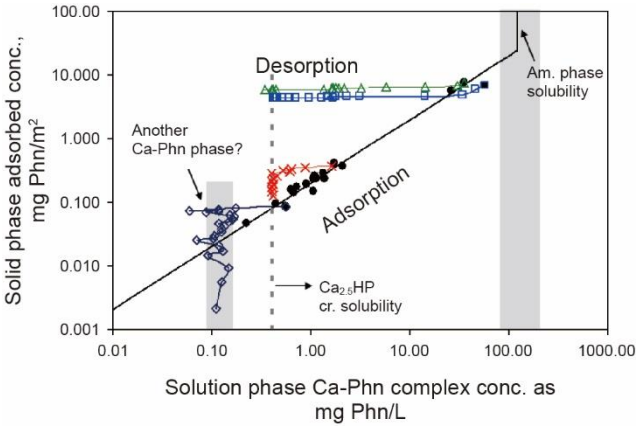


Fig. S2

All of these laboratory and field curves (above and numerous other lab and field data sets) can be modeled with one unified model that is a function of measured parameters for any squeeze and the connate formation water composition. Each phase is represented by a solubility constant that depends on temperature and ionic strength. The similarity of crystalline $Ca_{2.5}HNTMP$ and crystalline $Ca_5(PO_4)_3OH$ (HAP) is seen in Table S3.

Table S3

Solid phase	pK_{sp}, 158 ºF & 1 M Ionic strength	Root mean = pKsp/(no. of ions)
$Ca_5(PO_4)_3OH$	48.79	5.42 (= 48.79/9)
$Ca_{2.5}HNTMP$	24.2	5.38 (= 24.2/4.5)

With this model the return data from the following eight wells were simulated, with results in Tables S4 and S5.

Table S4 The produced water composition of the eight wells studied by the research group of the present authors

Well Name	Gladys McCall	Pleasant Bayou	O'Daniel No. 2	N. R. Smith	Huff A	High Island, A-9	Aramco A1	A. E. Guerra No. 43
Location	Grand Chenier, Cameron Parish, LA	Brazoria Co., TX	Galveston, TX	San Patricio Co., TX	Galveston Co., TX	Offshore, Galveston, GOM	Uthmaniyah, Saudi Arabia	Hidalgo, TX
Field	Geopressued-geothermal prospect	Geopressued-geothermal prospect	Alta Loma East	Odem	N.E. Hitchcock	32 Fathom	Ghawar	McAllen Ranch
Na^+ (mg/L)	32,941	50,255	16,100	19,069	16,181	25,100	14,270	19,872
Mg^{2+} (mg/L)	0	0	204	146	0	137	890	54
Ca^{2+} (mg/L)	4,130	9,600	760	480	448	1,230	4,000	6,500
Sr^{2+} (mg/L)	0	0	0	0	0	0	162	700
Ba^{2+} (mg/L)	0	0	52	19	21	84	l	550
Fe^{2+} (mg/L)	35	0	0	8	9	7	0	12
Cl^- (mg/L)	57,900	94,430	24,500	30,000	25,400	41,000	30,800	43,000
SO_4^{2-} (mg/L)	0	0	38	14	24	47	680	5
Total Alk (mg/L)	547	307	560	1,171	549	480	461	281
TDS (mg/L)	96,340	130,000	43,624	50,899	42,831	68,050	51,833	70,900
Density (STP)	1.06	1.08	1.03	1.03	1.03	1.04	1.03	1.05
CO_2 (%, STP)	7.60	8.00	1.00	1.55	0.50	2.29	10.00	0.27
pH	6.53	6.26	7.45	7.55	7.73	6.98	6.41	7.72
Gas/Day (MCF)	800	150	1,000	80	1,000	12,000	3,360	8,5000
Oil/Day (STB)	0	0	25	39	50	105	6000	50
Water/Day (STB)	30,000	23,000	4,000	2,300	3,600	400	9,600	100
B-H temperature (ºF)	320	305	285	160	210	282	195	340
W-H temperature (ºF)	270	270	240	130	190	190	158	120
B-H pressure (psia)	12,910	11,168	9,000	1,900	3,200	9,762	2,500	7,000
W-H pressure (psia)	250	500	300	100	160	5,000	150	400

Table S5 Detailed information about the squeeze procedure used for the eight wells studied by the research group of the present authors

Well	Gladys McCall	Pleasant Bayou	O'Daniel No. 2	N. R. Smith	Huff A	High Island, A-9	Aramco A-1	A.E. Guerra 43
Inhibitor	NTMP	NTMP	NTMP	NTMP	NTMP	NTMP	NTMP	NTMP/BHPMP
Preflush volume (bbl)	300	100	30	30	25	30	1000	
Inhibitor pill volume (bbl)	100	100	380	182	800	314	84	270
Active inhibitor concentration (%)	3	3	1.55	1.5	0.49	1.0	22.8	0.35
Acidity	Neutral	Neutral	Acid	Acid	Acid	Acid	Acid	Acid
Extra acid present (moles HCl/mol Inh)	-	-	0.19	0.19	0.19	0.19	0.19	0.19
Make-up Fluid	KCI	KCI	Field brine	Field brine	Field brine	Field brine	?	Field brine
KCl concentration (wt%)	10	10	-	-	-		7.4	-
Overflush volume (bbl)	900	1200	390	800	300	485	1432	250
Shut-in time (h)	24	36	48	48	24	48	48	48
Squeeze life (days)	600	87	365	591	455	-	2,610	438

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