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SUPPORTING INFORMATION

Impacts of Antiscalants on the Formation of Calcium Solids:

Implication on Scaling Potential of Desalination Concentrate

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Figure S1 Molecular structures of the three most widely used phosphonic antiscalants that are examined in this study.

NTMP: nitrilotris(methylenephosphonic acid);

EDTMP: ethylenediaminetetra(methylenephosphonic acid);

DTPMP: diethylenetriaminepenta(methylenephosphonic acid)



Figure S2 The negligible effect of tris(hydroxymethyl)aminomethane (TRIS) pH buffer concentration on the precipitation of Ca₅(PO₄)₃OH_(s) in presence of antiscalant EDTMP. Results showed that the presence of different TRIS buffer concentrations did not affect the precipitation kinetics. $[Ca^{2+}] = 10 \text{ mM}$; $[PO_4^{3-}] = 31 \text{ mg P/L}$; saturation index = 14.8; $[EDTMP] = 3 \mu M$; pH = 7.8; ionic strength = 100 mM.

Text S1 Kinetics modeling of the precipitation of calcium solids

The backbone of the model is the Michaelis-Menten equation that gives the relationship between the turbidity of the precipitation and the time of the precipitation reaction (Eqn. 1):

$$T = T_{\max} \frac{t}{t + K_{\mathrm{m}}} \tag{1}$$

Where, *T* is the turbidity of the precipitation (NTU) at time *t* (seconds), T_{max} is the maximum turbidity of the precipitation reaction (NTU) and K_{m} is the Michaelis-Menten half-velocity constant (seconds).

Figure S3A shows the experimental data for the precipitation of hydroxyapatite in absence of antiscalant with time. The Michaelis-Menten type of model as described in equation 1 above is fit for the rapid-precipitation stage of the reaction. The constant, T_{max}/K_m gives the rate constant of the precipitation (NTU/second). This kinetic model fits the precipitation of all calcium solids very well. Figure S3B shows a typically data fitting on the precipitation of hydroxyapatite with different NTMP and phosphate dosages.



Figure S3 (A) Kinetic modeling on the precipitation of $Ca_5(PO_4)_3OH_{(s)}$. $[Ca^{2+}] = 10 \text{ mM}$; $[PO_4^{3-}] = 22 \text{ mg P/L}$; saturation index = 14.3; $[NTMP] = 0 \mu M$; pH = 7.8; [TRIS buffer] = 20 mM; ionic strength = 100 mM. (B) Michaelis-Menten model fitting for precipitation of $Ca_5(PO_4)_3OH_{(s)}$ at different saturation indices in the presence of varying dosages of NTMP. $[Ca^{2+}] = 10 \text{ mM}$; $[PO_4^{3-}] = 20-32 \text{ mg P/L}$; saturation index = 14.3-14.9; $[NTMP] = 0-6 \mu M$; pH = 7.8; ionic strength = 100 mM; [TRIS buffer] = 20 mM.



Figure S4 X-ray diffraction of precipitated solids. Three scale-forming calcium solids were confirmed. (A) gypsum, (B) vaterite, (C) hydroxyapatite.

Text S2 Calculations on calcium complexation with different antiscalants

Mass balance for total calcium gives the equation below:

$$TOTCa = \{Ca^{2+}\} + \{CaHL\}^{3-} + \{CaH_2L\}^{2-} + \{CaH_3L\}^{-} + \dots + \{CaH_iL\}^{i-4} + \{CaOH\}^{+}$$
(2)

Where *TOT*Ca is the total dissolved calcium concentration, and L is the Ligand (NTMP in the above case, which has a negative six charges for its most deprotonated species L).

$$\beta_i = \frac{\{CaH_{i-1}L\}}{\{Ca^{2+}\}\{H\}^{(i-1)}\{L\}}$$
(3)

The speciation equilibrium for CaOH⁺, which has a p K_a of 12.7 (Visual MINTEQ) is calculated as below:

$$\{CaOH^+\} = \{Ca^{2+}\} \frac{10^{-12.7}}{\{H^+\}}$$
(4)

In addition, calcium-antiscalant complexes for NTMP, EDTMP and DTPMP are listed in Table S1.

$$TOTCa = \{Ca^{2+}\} \left(1 + \left\{ \frac{CaL^{4-}}{Ca^{2+}} \right\} + \left\{ \frac{CaHL^{3-}}{Ca^{2+}} \right\} + \left\{ \frac{CaH_2L^{2-}}{Ca^{2+}} \right\} + \left\{ \frac{CaH_3L^{-}}{Ca^{2+}} \right\} + \left\{ \frac{CaH_4L}{Ca^{2+}} \right\} + \left\{ \frac{CaOH^+}{Ca^{2+}} \right\} \right)$$
(5)

$$TOTCa = \{Ca^{2+}\} \left(1 + \beta_1 \{L\} + \beta_2 \{H^+\} \{L\} + \beta_3 \{H^+\}^2 \{L\} + \beta_4 \{H^+\}^3 \{L\} + \beta_5 \{H^+\}^4 \{L\} + \frac{K}{\{H^+\}} \right)$$
(6)

Let
$$\left(1 + \beta_1 \{L\} + \beta_2 \{H^+\} \{L\} + \beta_3 \{H^+\}^2 \{L\} + \beta_4 \{H^+\}^3 \{L\} + \beta_5 \{H^+\}^4 \{L\} + \frac{\kappa}{\{H^+\}}\right) = B$$

$$\alpha_{\rm Ca^{2+}} = \frac{1}{B} \tag{7}$$

$$\alpha_{\text{CaL}^{4-}} = \frac{\beta_1 \{L\}}{B} \tag{8}$$

$$\alpha_{\text{CaHL}^{3-}} = \frac{\beta_2 \{\text{H}^+\}\{\text{L}\}}{B}$$
(9)

$$\alpha_{\rm CaH_2L^{2-}} = \frac{\beta_3 \{\rm H^+\}^2 \{\rm L\}}{B}$$
(10)

$$\alpha_{\text{CaH}_3\text{L}^-} = \frac{\beta_4 \{\text{H}^+\}^3 \{\text{L}\}}{B} \tag{11}$$

$$\alpha_{\text{CaH}_{4}\text{L}} = \frac{\beta_{5}\{\text{H}^{+}\}^{4}\{\text{L}\}}{B}$$
(12)

$$\alpha_{CaOH^+} = \frac{K}{\{H^+\}B} \tag{13}$$

Where, $\alpha_{Ca^{2+}}$, $\alpha_{CaL^{4-}}$, $\alpha_{CaHL^{3-}}$, $\alpha_{CaH_2L^{2-}}$, $\alpha_{CaH_3L^{-}}$, α_{CaH_4L} and α_{CaOH^+} is the fraction of total dissolved calcium existing as Ca²⁺, CaL⁴⁻, CaHL³⁻, CaH₂L²⁻, CaH₃L⁻, CaH₄L and CaOH⁺, respectively.

The fraction of total dissolved calcium existing as Ca^{2+} as a function of solution pH is plotted in Figure S4.

#	Calcium ligand complexes with NTMP	$\mathrm{Log}eta_i$ a
(1)	$Ca^{2+} + L^{6-} \leftrightarrow CaL^{4-}$	7.6
(2)	$Ca^{2+} + H^+ + L^{6-} \leftrightarrow CaHL^{3-}$	16.6
(3)	$Ca^{2+} + 2H^+ + L^{6-} \leftrightarrow CaH_2L^{2-}$	22.9
(4)	$Ca^{2+} + 3H^+ + L^{6-} \leftrightarrow CaH_3L^-$	28
(5)	$Ca^{2+} + 4H^+ + L^{6-} \leftrightarrow CaH_4L$	32.1
	Calcium ligand complexes with EDTMP	$\mathrm{Log}eta_i$ b
(6)	$Ca^{2+} + L^{6-} \leftrightarrow CaL^{4-}$	9.29
(7)	$Ca^{2+} + H^+ + L^{6-} \leftrightarrow CaHL^{3-}$	18.74
(8)	$Ca^{2+} + 2H^+ + L^{6-} \leftrightarrow CaH_2L^{2-}$	26.98
(9)	$Ca^{2+} + 3H^+ + L^{6-} \leftrightarrow CaH_3L^-$	33.72
(10)	$Ca^{2+} + 4H^+ + L^{6-} \leftrightarrow CaH_4L$	39.21
	Calcium ligand complexes with DTPMP	L og K °
(11)	$Ca^{2+} + H_1^{8-} \leftrightarrow CaH_1^{6-}$	<u> </u>
(11) (12)	$Ca^{2+} + H_1 I^{7-} \leftrightarrow CaH_1 I^{5-}$	4 41
(12) (13)	$Ca^{2+} + H I^{6-} \leftrightarrow Ca H I^{4-}$	3 78
(13) (14)	$Ca^{2+} \perp H_{1} L^{5-} \leftrightarrow CaH_{1} L^{3-}$	3.5
(1+) (15)	$Ca^{2+} \perp H I^{4-} \leftarrow CaH I^{2-}$	2 52
(15) (16)	$Ca^{2+} \perp H I^{3-} \hookrightarrow CaH I^{-}$	1 89
(10) (17)	$Ca^{2+} + HI^{2-} \leftrightarrow CaHI$	1.89
(17) (18)	$Ca + H_8L \leftrightarrow CaH_8L$ $Ca^{2+} + H_1^+ \leftrightarrow CaH_1^+$	0.63
(10)		0.05
	Calcium hydroxy complex	LogK ^c
(19)	$Ca^{2+} + H_2O \leftrightarrow CaOH^+ + H^+$	-12.697

 Table S1 Calcium-antiscalant complexes and their stability constants.

^a Taken from reference (1), ^b Taken from reference (2), ^c Taken from reference (3).



Figure S5 The impact of pH on the fraction of total dissolved calcium existing as free calcium in the presence of each antiscalant.

Text S3 Calculations for net charge of different antiscalants at different pH

Mass balance on the speciation of an antiscalant gives the equation below:

$$TOTL = L^{6-} + \{HL\}^{5-} + \{H_2L\}^{4-} + \{H_3L\}^{3-} + \dots + \{H_iL\}^{(n-i)-}$$
(14)

where L^{6-} is the most deprotonated form of NTMP. *TOT*L is defined as the sum of the concentration of all the species in the solution that contain an antiscalant, *n* is the charge of the most deprotonated species and *i* varies from 0 to *n*.

Speciation constants for NTMP, EDTMP and DTPMP are shown in Table S2 below.

	· · · · · · · · · · · · · · · · · · ·	
#	NTMP	$\mathrm{p}K_a$ d
(1)	$H_5L^- + H^+ \leftrightarrow H_6L$	0.30
(2)	$H_4L^{2-} + H^+ \leftrightarrow H_5L^-$	1.50
(3)	$H_3L^{3-} + H^+ \leftrightarrow H_4L^{2-}$	4.64
(4)	$H_2L^{4-} + H^+ \leftrightarrow H_3L^{3-}$	5.86
(5)	$\mathrm{HL}^{5-} + \mathrm{H}^{+} \leftrightarrow \mathrm{H}_{2}\mathrm{L}^{4-}$	7.30
(6)	$L^{6-} + H^+ \leftrightarrow HL^{5-}$	12.10
	EDTMP	$\mathrm{p}K_a$ e
(7)	$H_6L^- + H^+ \leftrightarrow H_7L$	1.30
(8)	$H_5L^{2-} + H^+ \leftrightarrow H_6L^-$	2.96
(9)	$H_4L^{3-} + H^+ \leftrightarrow H_5L^{2-}$	5.12
(10)	$H_3L^{4-} + H^+ \leftrightarrow H_4L^{3-}$	6.40
(11)	$H_2L^{5-} + H^+ \leftrightarrow H_3L^{4-}$	7.87
(12)	$HL^{6-} + H^+ \leftrightarrow H_2L^{5-}$	7.85
(13)	$L^{7-} + H^+ \leftrightarrow HL^{6-}$	13.01
	DTPMP	pK _a f
(14)	$H_9L^- + H^+ \leftrightarrow H_{10}L$	1.04
(15)	$H_8L^{2-} + H^+ \leftrightarrow H_9L^-$	2.08
(16)	$H_7L^{3-} + H^+ \leftrightarrow H_8L^{2-}$	3.11
(17)	$H_6L^{4-} + H^+ \leftrightarrow H_7L^{3-}$	4.15
(18)	$H_5L^{5-} + H^+ \leftrightarrow H_6L^{4-}$	5.19
(19)	$H_4L^{6-} + H^+ \leftrightarrow H_5L^{5-}$	6.23
(20)	$H_3L^{7-} + H^+ \leftrightarrow H_4L^{6-}$	7.23
(21)	$H_2L^{8-} + H^+ \leftrightarrow H_3L^{7-}$	8.30
(22)	$\mathrm{HL}^{9-} + \mathrm{H}^+ \leftrightarrow \mathrm{H}_2 \mathrm{L}^{8-}$	11.18
(23)	$L^{10-} + H^+ \leftrightarrow H\bar{L}^{9-}$	12.58

Table S2 Protonation constants of NTMP, EDTMP and DTPMP

^d Taken from literature (4), ^e Taken from literature (2), ^f Taken from literature (5)

$$pK_{a,i} = -\log\left(\frac{\{H_{n-i+1}L\}^{1-i}}{\{H^+\}\{H_{n-i}L\}^{-i}}\right)$$
(15)

where L is the most deprotonated form of the ligand (NTMP, EDTMP or DTPMP), *n* is the charge of the most deprotonated form of the ligand (n = 6, 8 and 10 for NTMP, EDTMP and DTPMP, respectively) and *i* varies from 0 to *n*.

$$\alpha_{i} = \frac{\{\mathrm{H}^{+}\}^{n-i} \prod_{j=0}^{i} K_{aj}}{\sum_{k=0}^{n} (\{\mathrm{H}^{+}\}^{n-k} \prod_{j=0}^{k} K_{aj})}$$
(16)

Where α_i is defined as the fraction of *TOT*L that is in a form that has lost *i* protons, *n* is the number of protons in the most protonated state, $K_{a0} = 1.0$. Thus, for NTMP, the value of α for the species H₆L is defined as:

$$\alpha_0 = \frac{\{\mathrm{H}^+\}^6}{\{\mathrm{H}^+\}^6 + \{\mathrm{H}^+\}^5 K_{a1} + \{\mathrm{H}^+\}^4 K_{a1} K_{a2} + \dots + K_{a1} K_{a2} K_{a3} K_{a4} K_{a5} K_{a6}}$$
(17)

Using the pK_a values from Table S2 and equation (15), (16) and (17) the fraction of each species is calculated at different pHs. Accordingly, the net charge of each antiscalant molecule is calculated by using the equation below:

molecular charge per mole =
$$\sum_{i=0}^{i=n} \alpha_i z_i$$
 (18)

Where z_i is the charge of species that has lost *i* protons, *n* is the number of protons in the most protonated species.



Figure S6 The impact of pH on the charge of each antiscalant. The charge is normalized to the molar concentration of the antiscalant and shown as the ratio of charge to molar concentration of antiscalant in the y-axis.



Figure S7 Impact of the antiscalant DTPMP on the zeta potential of hydroxyapatite at different pHs. $[Ca^{2+}] = 10 \text{ mM}; [PO_4^{3-}] = 26 \text{ mg P/L};$ saturation index = 14.2; $[DTPMP] = 1 \mu M;$ ionic strength=100 mM; [TRIS buffer] = 20 mM.



Figure S8 The effect of EDTMP dosage on the extension of induction time for $CaSO_{4(s)}$ and $CaCO_{3(s)}$ precipitation. Experimental conditions: (A) $[Ca^{2+}] = 37-80$ mM; $[SO_4^{2-}] = 564$ mM; ionic strength = 1 M pH = 7.8. (B) $[Ca^{2+}] = 10$ mM; $[CO_3^{2-}] = 10-36$ mM; pH = 7.8; ionic strength = 100 mM; [TRIS buffer] = 50 mM.



Figure S9 The impact of varying dosage of EDTMP at different saturation indices on the induction time for $Ca_5(PO_4)_3OH_{(s)}$, $CaCO_{3(s)}$ and $CaSO_{4(s)}$ nucleation. (A) $[Ca^{2+}] = 10$ mM; $[PO_4^{3-}] = 18-30$ mg P/L; pH = 7.8; ionic strength = 100 mM; [TRIS buffer] = 20 mM. (B) $[Ca^{2+}] = 10$ mM; $[CO_3^{2-}] = 10-36$ mM; pH = 7.8; ionic strength = 100 mM; [TRIS buffer] = 50 mM. (C) $[Ca^{2+}] = 37-80$ mM; $[SO_4^{2-}] = 560$ mM; ionic strength = 1 M; pH = 7.8.



Figure S10 Impact of saturation index of $CaCO_{3(s)}$ and $CaSO_{4(s)}$ on activation energy of nucleation at varying EDTMP dose. (A) $[Ca^{2+}] = 10$ mM; $[CO_3^{2-}] = 10-36$ mM; pH = 7.8; ionic strength = 100 mM; [TRIS buffer] = 50 mM. (B) $[Ca^{2+}] = 37-80$ mM; $[SO_4^{2-}] = 564$ mM; pH = 7.8; ionic strength = 1 M.



Figure S11 Impact of saturation index of CaCO₃(s) and CaSO₄(s) on critical radius of nucleation at varying EDTMP dose. A: Experimental conditions for CaCO_{3(s)}: $[Ca^{2+}] = 10$ mM; $[CO_3^{2-}] = 10$ -36 mM; [EDTMP] = 0-21 μ M; pH = 7.8; Ionic strength = 100 mM; TRIS= 50 mM; B: Experimental conditions for CaSO_{4(s)}: $[Ca^{2+}] = 37$ -80 mM; $[SO_4^{2-}] = 564$ mM; [EDTMP] = 0-16 μ M; ionic strength = 1M; pH = 7.8.

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