

Electronic Supporting Information (ESI) for:
Mechanistic understanding of calcium-phosphonate solid dissolution
and scale inhibitor return behavior in oilfield reservoir:
Formation of middle phase

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1. DTPMP analysis methods:

DTPMP concentrations (above 3 mg L⁻¹) were analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES) (Optima 4300 DV, Perkin Elmer). The wavelength for phosphorus measurement was 213.617 nm. A solution containing 5 mg L⁻¹ yttrium (371.029 nm) was utilized as an internal standard solution. Each sample measurement was repeated for five times and the mean value of these measurements was reported. The standard deviation for every sample measurement was less than 0.5 %. Measurement of low concentrations of DTPMP was realized by digesting DTPMP to form phosphate and then producing the phosphomolybdenum blue complex and measuring spectrophotometrically at 890 nm (Ref. #1). Spectrophotometric method (HACH Co., Loveland, CO.) is able to measure phosphonate from as low as 0.1 to 2.5 mg L⁻¹ as phosphate, which corresponds to 0.12 to 3 mg L⁻¹ as DTPMP.

2. Experimental conditions and results of Ca-DTPMP precipitate experiments

Exp. No	Initial solution compositions before the precipitation tests				Experimental results after the precipitation tests		
	DTPMP species	Ca (mole Kg ⁻¹ H ₂ O)	DTPMP (mole Kg ⁻¹ H ₂ O)	Ca/DTPMP Molar Ratio	pH	Ca/DTPMP Molar Ratio in the solid	Appearance
1	H ₁₀ DTPMP	0.427	0.214	2	0.23	N.A.	clear gel
2	H ₁₀ DTPMP	0.660	0.220	3	0.19	N.A.	clear gel
3	H ₁₀ DTPMP	0.906	0.227	4	0.06	N.A.	clear gel
4	NaH ₉ DTPMP	0.210	0.210	1	0.58	N.A.	clear gel
5	NaH ₉ DTPMP	0.431	0.216	2	0.47	N.A.	clear gel
6	NaH ₉ DTPMP	0.667	0.222	3	0.39	N.A.	clear gel
7	NaH ₉ DTPMP	0.916	0.229	4	0.22	N.A.	clear gel
8	Na ₂ H ₈ DTPMP	0.212	0.212	1	1.22	N.A.	turbid gel
9	Na ₂ H ₈ DTPMP	0.436	0.218	2	1.06	N.A.	turbid gel
10	Na ₂ H ₈ DTPMP	0.674	0.225	3	0.81	N.A.	turbid gel
11	Na ₂ H ₈ DTPMP	0.854	0.213	4	0.78	N.A.	turbid gel
12	Na ₃ H ₇ DTPMP	0.214	0.214	1	2.27	N.A.	turbid gel
13	Na ₃ H ₇ DTPMP	0.440	0.220	2	1.88	N.A.	turbid gel
14	Na ₃ H ₇ DTPMP	0.681	0.227	3	1.72	N.A.	turbid gel
15	Na ₃ H ₇ DTPMP	0.862	0.216	4	1.6	N.A.	turbid gel
16	Na ₄ H ₆ DTPMP	0.216	0.216	1	3.36	2.14	White precipitant
17	Na ₄ H ₆ DTPMP	0.445	0.223	2	2.55	2.21	White precipitant
18	Na ₄ H ₆ DTPMP	0.697	0.232	3	2.08	2.31	White precipitant
19	Na₄H₆DTPMP	0.844	0.211	4	1.75	2.45	White precipitant
20	Na ₄ H ₆ DTPMP	1.076	0.215	5	1.9	2.50	White precipitant
21	Na ₅ H ₅ DTPMP	0.218	0.218	1	4.33	2.42	White precipitant
22	Na ₅ H ₅ DTPMP	0.450	0.225	2	2.94	2.63	White precipitant
23	Na ₅ H ₅ DTPMP	0.677	0.226	3	2.63	2.91	White precipitant
24	Na ₅ H ₅ DTPMP	0.822	0.205	4	2.31	3.21	White precipitant
25	Na ₆ H ₄ DTPMP	0.221	0.221	1	5.16	N.A.	Gel
26	Na ₆ H ₄ DTPMP	0.455	0.227	2	3.82	2.82	White precipitant
27	Na ₆ H ₄ DTPMP	0.658	0.219	3	3.09	3.33	White precipitant
28	Na ₆ H ₄ DTPMP	0.801	0.200	4	2.78	3.71	White precipitant
29	Na ₇ H ₃ DTPMP	0.223	0.223	1	5.88	N.A.	Gel
30	Na ₇ H ₃ DTPMP	0.460	0.230	2	5.40	N.A.	Gel
31	Na ₇ H ₃ DTPMP	0.641	0.214	3	3.58	3.94	White precipitant
32	Na ₇ H ₃ DTPMP	0.781	0.195	4	3.33	4.29	White precipitant

3. References:

1. A.T. Kan, J.E. Oddo and M.B. Tomson, Formation of Two Calcium Diethylenetriaminepentakis (methylene phosphonic acid) Precipitates and Their Physical Chemical Properties, Langmuir, 1994, 10, 1450.