

**Electronic Supporting Information (ESI) for:**  
**Phosphino-polycarboxylic acid modified inhibitor nanomaterial for oilfield  
scale control: Transport and inhibitor return in formation media**

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## **1. Synthesis of PPCA modified calcium-DTPMP SINM and nanofluid:**

The below paragraph on nanofluid synthesis was adopted from Ref. #1 Experimental Section:

A DTPMP solution (0.1 mole per kg water) was prepared by diluting the acidic DTPMP stock solution with DI water and the solution pH was adjusted to 11.3 with 10 M NaOH. CaCl<sub>2</sub> solution (0.4 mole per kg water) was prepared in DI water. PPCA solution (0.2% wt./wt.) was prepared by diluting the stock PPCA solution with DI water and adjusted to 7.0 pH with 2 M NaOH. In a typical synthesis experiment, 100 mL DI water was added into a 250 mL two-neck flask and heated to 90°C in a water bath. While the DI water inside the flask was stirred at 90°C, CaCl<sub>2</sub> solution (25 mL) and DTPMP solution (25 mL) were simultaneously added dropwise into the flask using a syringe pump (Harvard Apparatus Inc.). Immediately upon injection of CaCl<sub>2</sub> and DTPMP, white Ca-DTPMP precipitates formed from the aqueous solution. The addition of CaCl<sub>2</sub> and DTPMP solutions was generally completed within 2 min and the mixture was stirred for an additional 1.5 min before the mixture was air cooled to room temperature (22°C). Upon the completion of solution addition and subsequent cooling, a white suspension was obtained with a final pH of ca. 7.2. Subsequently, the white suspension was centrifuged at 6,500 rpm for 10 minutes. After discarding the supernatant solution, the solid sample was washed by DI water to remove the salt and saved as a wet paste. Ca-DTPMP nanomaterial suspension (nanofluid) was prepared by re-dispersing the obtained Ca-DTPMP paste into a PPCA solution (0.2% wt./wt.) via an ultrasonication method. Typically, 1 g of the prepared Ca-DTPMP solid was dispersed into a 100 mL solution of PPCA or PPCA/KCl solution. In this study, the ultrasonication treatment involves a probe sonicator (Sonics & Materials Inc.) and a sonication bath (Model FS-14, Fisher Scientific). As a comparison, the formed Ca-DTPMP wet paste was also sonication treated in DI water free of PPCA. The inhibitor DTPMP loading in the tested nanofluid was about 0.8% (wt./wt.).

## 2. DTPMP analysis methods:

DTPMP concentrations (above 3 mg L<sup>-1</sup>) 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<sup>-1</sup> 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.<sup>2</sup> Spectrophotometric method is able to measure phosphonate from as low as 0.1 to 2.5 mg L<sup>-1</sup> as phosphate, which corresponds to 0.12 to 3 mg L<sup>-1</sup> as DTPMP.

## 3. Measurement results of SINM zeta potential

Experiment #	PPCA (% wt./wt.)	KCl (% wt./wt.)	Sonication Treatment	Zeta potential (mV)
1	0.2	0	bath	-30
2	0.2	0.2	bath	-22
3	0.2	0.5	bath	-18
4	0.2	1	bath	Near neutral <sup>a</sup>
5	0.2	1	probe	Near neutral <sup>a</sup>
6	2	0.3	probe	Near neutral <sup>a</sup>
7	1	0.4	probe	Near neutral <sup>a</sup>

<sup>a</sup>. zeta potential for Sample #4 to #7 were not reported due to the unrepeatable measurement results of near neutral zeta potential values.

## 4. Understanding the SINM transport via advection and diffusion mechanism:

### 4.1 Theory

From the standpoint of advection and diffusion, the transport of inhibitor nanofluid can be mathematically described by one dimensional advection dispersive equation:<sup>3-5</sup>

$$R \frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + v \frac{\partial C}{\partial x} + J_d C = 0 \quad (\text{Eq. ESI-1})$$

$C$  (mg L<sup>-1</sup>) is the effluent SINM concentration at a given time;  $t$  (min) is the time;  $D$  (cm<sup>2</sup> min<sup>-1</sup>) is the hydrodynamic dispersion coefficient;  $x$  (cm) accounts for the distance of SINM transport inside the column; and  $v$  (cm min<sup>-1</sup>) is the linear pore velocity calculated as  $v=Q/\pi r^2 \varepsilon$ , where  $Q$  is the flow rate (mL min<sup>-1</sup>);  $\varepsilon$  is the sandstone medium porosity, and  $r$  (cm) is the cross sectional radius of the column bed. Linear pore velocity is the average travel velocity for SINM particles. The first term of Eq. ESI-1 is the SINM concentration change at a given time; the second term is the change in concentration due to diffusion/dispersion; the third term represents SINM concentration change associated with advection and the last term is the SINM mass removal modeled as a first order deposition process.<sup>3-5</sup> The mathematical solution to Eq. ESI-1 can be expressed as:<sup>3-5</sup>

$$C(x, t) = \frac{1}{2} \exp\left[\frac{(v-w)x}{2D}\right] \text{erfc}\left[\frac{Rx-wt}{2(DRt)^{0.5}}\right] + \frac{1}{2} \exp\left[\frac{(v+w)x}{D}\right] \text{erfc}\left[\frac{Rx+wt}{2(DRt)^{0.5}}\right] \quad (\text{Eq. ESI-2})$$

and  $w = (v^2 + 4J_d D)^{0.5}$

Thus, based on Eq. ESI-2, the breakthrough level ( $C/C_0$ ) of the SINM particles from the column transport experiment can be mathematically calculated and compared with the experimentally obtained breakthrough level. The values of  $R$  and  $J_d$  in each transport study were acquired by minimizing the differences between the calculated effluent concentrations based on Eq. ESI-2 and the experimentally observed effluent concentrations via the least square method. Excel Solver function was used to find the  $R$  and  $J_d$  values.

## 4.2 Characterization of calcite formation medium via tracer test

A tracer (tritiated water) test was carried out to measure the PV and the hydrodynamic dispersion coefficient (D) of the packed column. According to the breakthrough curves of the tracer in each medium, the D values for each medium can be obtained by fitting the one-dimensional advection-dispersion equation (Eq. 1) to the acquired data using CXTFIT code,<sup>6</sup> by setting the retardation factor (R) to one:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (\text{Eq. ESI-3})$$

where C (mg L<sup>-1</sup>) is the effluent nanomaterials concentration at a certain time; t (min) denotes the time. The tracer test was conducted at a flow rate of 60 mL hr<sup>-1</sup>, corresponding to a pore velocity of 2 cm min<sup>-1</sup> and the measured D value is 0.065 cm<sup>2</sup> min<sup>-1</sup>.

## 5. Understanding the SINM transport via filtration and attachment mechanism:

The transport of SINM particles is a course of the particles being continuously removed by sandstone medium via collection and attachment of SINM particles to sandstone surfaces. The deposition of SINM particles to sandstone medium surface includes two steps: collection of SINM particles by medium surfaces (particle collection) and subsequent attachment of the SINM particles to medium surface (particle attachment).<sup>4</sup> Therefore, a collection efficiency ( $\eta_0$ ) and an attachment efficiency ( $\alpha$ ) were introduced to describe the particle collection and attachment processes, respectively. The collection efficiency ( $\eta_0$ ) considers the particle collection due to Brownian diffusion, interception and sedimentation. Thus, the  $\eta_0$  term can be expressed as the sum of these three mechanisms:<sup>3-5</sup>

$$\eta_0 = \eta_D + \eta_I + \eta_G \quad (\text{Eq. ESI-4})$$

where  $\eta_D$ ,  $\eta_I$  and  $\eta_G$  are the single collector efficiency components due to Brownian diffusion, interception and sedimentation, respectively. Typically, the Brownian diffusion will be dictating the collection of submicron sized particles to the medium surface within the particle size range of 1  $\mu\text{m}$ .<sup>4,5</sup>

These three components can be calculated as a function of several dimensionless groups as follows:<sup>4,5,7</sup>

$$\eta_D = 2.4A_s^{1/3} N_R^{-0.081} N_{pe}^{-0.715} N_{vdW}^{-0.052} \quad (\text{Eq. ESI-5})$$

where  $A_s$  is the porosity-dependent parameter of Happel's model,  $N_R$  is the aspect ratio,  $N_{pe}$  is the Peclet number, and  $N_{vdW}$  is the van der Waals number.  $A_s$  is the porosity-dependent parameter of Happel's model and is defined as:

$$A_s = \frac{2(1 - \gamma^5)}{2 - \gamma + 3\gamma^5 - 2\gamma^6} \quad (\text{Eq. ESI-6})$$

where  $\gamma = (1 - \varepsilon)^{1/3}$ ,  $\varepsilon$  is the porosity of the porous medium.  $N_R$  is the ratio of particle diameter ( $d_p$ ) to spherical collector diameter ( $d_c$ ) (i.e.  $N_R = \frac{d_p}{d_c}$ ).

$$N_{pe} = \frac{vd_c}{D_\infty} \quad (\text{Eq. ESI-7})$$

where  $v$  ( $\text{m s}^{-1}$ ) is the pore velocity,  $D_\infty$  ( $\text{m}^2 \text{s}^{-1}$ ) is the diffusion coefficient in an infinite medium, which, according to Stocks-Einstein relation, is defined as:

$$D_\infty = \frac{kT}{3\pi\mu d_p} \quad (\text{Eq. ESI-8})$$

where  $k$  is the Boltzmann constant ( $1.38 \times 10^{-23} \text{ J K}^{-1}$ );  $T$  (K) is the absolute temperature;  $\mu$  ( $\text{kg m}^{-1} \text{ s}^{-1}$ ) is the absolute viscosity of the fluid (water). The van der Waals number  $N_{vdW}$  is defined as:

$$N_{vdW} = \frac{A}{kT} \quad (\text{Eq. ESI-9})$$

where A is the Hamaker constant (assumed to be  $10^{-20}$  J). Moreover,

$$\eta_I = 0.55A_s N_R^{1.55} N_{pe}^{-0.125} N_{vdW}^{0.125} \quad (\text{Eq. ESI-10})$$

$$\eta_G = 0.475 N_R^{-1.35} N_{pe}^{-1.11} N_{vdW}^{0.053} N_{gr}^{1.11} \quad (\text{Eq. ESI-11})$$

where  $N_{gr}$  is the gravitational force number, defined as:

$$N_{gr} = \frac{d_p^4 (\rho_p - \rho_f) g}{3kT} \quad (\text{Eq. ESI-12})$$

where  $\rho_p$  is the density of the nanoparticles;  $\rho_f$  is the density of fluid and g is the gravitational acceleration,  $9.81 \text{ m s}^{-2}$ .

## 6. Notes and references:

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