

Electronic Supporting Information (ESI) for:
Transport and return of oilfield scale inhibitor reverse micelle nanofluid:
Impact of preflush and overflow

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1. Synthesis of Calcium-DTPMP reverse micelle nanofluid:

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

In a typical synthesis reaction, approximately 10 g of AOT solution and 4 g of C12EO9 solution were added into 100 mL isooctane solution in a 150 mL glass beaker, followed by constant stirring for 15 min to prepare the surfactant mixture solution. Then, in a 100 mL glass baker 5 mL of an aqueous solution containing 0.16 M CaCl_2 and 0.02 M MES was added dropwise to 50 mL of the prepared surfactant mixture solution, while constantly stirred at room temperature (21°C). A clear translucent solution containing CaCl_2 RM can be obtained. Similarly, in another 100 mL glass beaker 5 mL of an aqueous solution of 0.04 M DTPMP with sodium chloride (pH=9.0, neutralized by 2.0 M NaOH) was added dropwise to 50 mL of the prepared surfactant mixture solution, while constantly stirred at room temperature. A clear translucent solution containing Na-DTPMP RM was obtained. Ca-DTPMP RMNF was prepared by mixing the previously obtained CaCl_2 RM solution with Na-DTPMP RM solution in a 200 mL glass beaker with stirring at room temperature and a translucent solution was obtained. Upon completion of the solution mixing, the resultant Ca-DTPMP RMNF was filtered through a 1 μm filter (Merck Millipore Corp.) to remove any undissolved particles. The resultant solution is Ca-DTPMP RMNF with a pH value of ca. 5.8. The nanofluid was centrifuged at 6,500 rpm for 10 min and little deposit was found at the bottom of the solution.

2. 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.² Spectrophotometric method 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.

3. Understanding the RMNF transport via advection and diffusion mechanism:

3.1 Theory

From the standpoint of advection and diffusion, the transport of inhibitor nanofluid can be mathematically described by one dimensional advection dispersive equation:³⁻⁵

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

C (mg L⁻¹) is the effluent RMNF concentration at a given time; t (min) is the time; D (cm² min⁻¹) is the hydrodynamic dispersion coefficient; x (cm) accounts for the distance of RMNF transport inside the column; and v (cm min⁻¹) is the linear pore velocity calculated as $v=Q/\pi r^2 \varepsilon$, where Q is the flow rate (mL min⁻¹); ε is the sandstone medium porosity, and r (cm) is the cross sectional radius of the column. Linear pore velocity is the average travel velocity for RMNF particles. The first term of Eq. ESI-1 is the RM concentration change at a given time; the second term is the change in concentration due to diffusion/dispersion; the third term represents RM concentration change associated with advection and the last term is the RM mass removal modeled as a first order deposition process.³⁻⁵ The mathematical solution to Eq. ESI-1 can be expressed as:³⁻⁵

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

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

Thus, based on Eq. ESI-2, the breakthrough level (C/C_0) of the RM 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.

3.2 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,⁶ by setting R to one and J_d to zero:

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

where C (mg L^{-1}) is the effluent tracer concentration at a certain time; t (min) denotes the time. The tracer test was conducted at a flow rate of 60 mL hr^{-1} , corresponding to a pore velocity of 2.85 cm min^{-1} and the measured D value is $0.065 \text{ cm}^2 \text{ min}^{-1}$. D value ($\text{cm}^2 \text{ min}^{-1}$) can be calculated as:

$$D = \alpha_d \times v \quad (\text{Eq. ESI-4})$$

where α_d (cm) is the dispersivity and v (cm min^{-1}) is the linear pore velocity introduced above. Based on Eq. ESI-4, α_d for calcite medium at 2.85 cm min^{-1} pore velocity is calculated to be 0.0228 cm . α_d is a characteristic property of a formation media³. Thus, the dispersivity of calcite should be maintained the same for different pore velocities. The D values for other flow velocities can be easily calculated as the product of the dispersivity with the pore velocity, as shown in Table 1 of the main article.

4. Understanding the RMNF transport via filtration and attachment mechanism:

The transport of RMNF particles is a course of the particles being continuously removed by sandstone medium via collection and attachment of RMNF particles to sandstone surfaces. The deposition of RMNF particles to sandstone medium surface includes two consecutive steps: collection of RMNF particles by medium surfaces (particle collection) and subsequent attachment of the RMNF particles to medium

surface (particle attachment).⁴ Therefore, a collection efficiency (η_0) and an attachment efficiency (α) were introduced to describe the particle collection and attachment processes, respectively. The collection efficiency (η_0) considers the particle collection due to Brownian diffusion, interception and sedimentation. Thus, the η_0 term can be expressed as the sum of these three mechanisms:³⁻⁵

$$\eta_0 = \eta_D + \eta_I + \eta_G \quad (\text{Eq. ESI-5})$$

where η_D , η_I and η_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 μm .^{4,5}

These three components can be calculated as a function of several dimensionless groups as follows:^{4,5,7}

$$\eta_D = 2.4A_s^{1/3}N_R^{-0.081}N_{pe}^{-0.715}N_{vdW}^{-0.052} \quad (\text{Eq. ESI-6})$$

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

$$A_s = \frac{2(1-\gamma^5)}{2-\gamma+3\gamma^5-2\gamma^6} \quad (\text{Eq. ESI-7})$$

where $\gamma = (1-\epsilon)^{1/3}$, ϵ 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. $N_R = \frac{d_p}{d_c}$).

$$N_{pe} = \frac{vd_c}{D_\infty} \quad (\text{Eq. Eq. ESI-8})$$

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

$$D_{\infty} = \frac{kT}{3\pi\mu d_p} \quad (\text{Eq. ESI-9})$$

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

$$N_{\text{vdW}} = \frac{A}{kT} \quad (\text{Eq. ESI-10})$$

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

$$\eta_I = 0.55A_s N_R^{1.55} N_{pe}^{-0.125} N_{\text{vdW}}^{0.125} \quad (\text{Eq. ESI-11})$$

$$\eta_G = 0.475N_R^{-1.35} N_{pe}^{-1.11} N_{\text{vdW}}^{0.053} N_{gr}^{1.11} \quad (\text{Eq. ESI-12})$$

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

$$N_{gr} = \frac{d_p^4(\rho_p - \rho_f)g}{3kT} \quad (\text{Eq. ESI-13})$$

where ρ_p is the density of the nanoparticles; ρ_f is the density of fluid and g is the gravitational acceleration, 9.81 m s^{-2} .

5. Calculation of negative logarithm of ion activity product:

As discussed previously,^{8, 9} phosphonate inhibitors are retained in calcite-bearing formation by forming metal-phosphonate salts. Thus, the release of phosphonate from Ca-phosphonate solid complexes during inhibitor return is proposed to be controlled by the dissolution of Ca-phosphonate precipitates into the production brine. Therefore, the course of Ca-DTPMP RM return of DTPMP can be viewed as a continuous dissolution of Ca-DTPMP solid complex into the synthetic brine. In light of a proposed solution-speciation model,¹⁰ the DTPMP return profiles can be delineated by calculating the negative logarithm of ion activity product (pIP) of the Ca-DTPMP complex. pIP can be calculated as:

$$pIAP = -\log_{10}[(Ca^{2+})^3 \{H^+\}^4 (DTPMP^{10-})] \quad (\text{Eq. ESI-14})$$

where parentheses accounts for molar concentration and braces for activity. The free calcium ion (Ca^{2+}) and $DTPMP^{10-}$ species concentrations were calculated from the total DTPMP concentrations in aqueous phase via a speciation model.¹⁰

6. Calculation of NSL and Protection volume

Normalized squeeze lifetime (NSL) is the ratio of inhibitor return volumes and the mass of inhibitors (DTPMP) injected.¹¹ NSL evaluates the volume of produced water protected for each kilogram of inhibitor added. Thus, NSL (bbl. kg^{-1}) can be calculated as:

$$NSL = \frac{\text{Return volume (liter)} \times 10^6 (\text{mg kg}^{-1})}{\text{Inhibitor mass (mg)} \times 159 (\text{liter bbl.}^{-1})} \quad (\text{Eq. ESI-15})$$

Protection volume is the estimated volume of production brine protected by injecting RMNF containing 1000 kg of DTPMP in a single squeeze treatment. Basically, protection volume (in the unit of bbl.) can be calculated as

$$\text{Protection volume} = NSL (\text{bbl. kg}^{-1}) \times 1000 \text{ kg} \quad (\text{Eq. ESI-16})$$

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