Electronic Supporting Information for:

Functional scale inhibitor nanoparticle capsule delivery vehicles for oilfield mineral scale control

Ping Zhang [a] *, Gedeng Ruan [a], Amy T. Kan [a, b] and Mason B. Tomson [a, b] *

[a] Department of Civil and Environmental Engineering,

Rice University, Houston, Texas

[b] Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment,

Rice University, Houston, Texas

Manuscript prepared for *RSC Advances*

* To whom correspondence should be addressed: ping.zhang@alumni.rice.edu and mtomson@rice.edu

1. Charge ratio (C_R) calculation:

Charge ratio (CR) is defined as:[1-3]

$$C_R = \frac{[amion]\times|z_-|}{[polymer]\times|z_+|} \qquad \text{(Eq. ESI-1)}$$

where z_- is the negative charge per anion and z_+ is the positive charge per chain of polyamine. Since DTPMP molecule is in the form of H_4DTPMP^{6-}, z_- is 6 for DTPMP. Each chain of PAH has one positive charge thus z_+ is 1. Considering a PAH solution concentration of 1 mg mL^{-1} and the molecular weight of each chain is 93.5 g $mole^{-1}$, PAH concentration is calculated to be 0.0107 M. DTPMP concentration is 0.1 M. Recognizing the volume of PAH solution is 15 mL and the volume of DTPMP is 1 mL, C_R can be easily calculated as 3.7.

2. Understanding the SINC particle transport via advection and diffusion mechanism

2.1 Theory

From the standpoint of advection and diffusion, the transport of inhibitor nanofluid can be mathematically described by a one-dimensional advection dispersive equation:[4-6]

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

C (mg L^{-1}) is the effluent SINC concentration at a given time; t (min) is the time; D (cm^2 min^{-1}) is the hydrodynamic dispersion coefficient; x (cm) accounts for the distance of SINC 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 bed. Linear pore velocity is the average travel velocity for SINC particles. The first term of Eq. ESI-2 is the SINC concentration change at a given time; the second term is the change in concentration due to diffusion/dispersion; the third term represents SINC concentration change associated with advection and the last term is the SINC particle mass removal modeled as a first order deposition process.[4] 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.

2.2 Characterization of sandstone medium via tracer breakthrough test

A tracer (tritiated water) test was carried out to measure the pore volume and the hydrodynamic dispersion coefficient (D) ($cm^2\ min^{-1}$) of the packed column. According to the breakthrough curves of the tracer in sandstone medium, the D values can be obtained by fitting the one-dimensional advection-dispersion equation (Eq. ESI-2) (without the last term) to the acquired data using CXTFIT code[7], by setting the retardation factor (R) to one:

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

where C ($mg\ L^{-1}$) is the effluent nanomaterials concentration at a certain time; t (min) denotes the time. The obtained D value is 0.07 $cm^2\ min^{-1}$ at a pore velocity of 4.5 cm min^{-1}. Dispersion coefficient ($cm^2\ min^{-1}$) is the product of dispersivity (cm) with pore velocity (cm min^{-1}).

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

where α_d (cm) is the dispersivity. α_d for sandstone medium at 4.5 cm min^{-1} pore velocity is calculated to be 0.0156 cm (156 µm). Dispersivity is a characteristic property of a media[4]. Thus, the dispersivity of Louise sandstone should be maintained the same at different pore velocities. By assuming the same dispersivity of 0.0156 cm, the D value for TE #7 (pore velocity of 2.4 cm min^{-1}) is calculated to be 2.4 * 0.0156 = 0.037 $cm^2\ min^{-1}$.

3. Understanding the SINC transport via filtration and attachment mechanism:

The transport of SINC particles is a course of the particles being continuously removed by sandstone medium via collection and attachment of SINC particles to sandstone surfaces. The deposition of SINC particles to sandstone medium surface includes two consecutive steps: collection of SINC particles by medium surfaces (particle collection) and subsequent attachment of the SINC particles to medium surface (particle attachment).[5] 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:[4-6]

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

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.[5, 6]

These three components can be calculated as a function of several dimensionless groups as follows[8]:

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

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:

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

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

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

where v (m s^{-1}) is the pore velocity, D_∞ (m^2 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 × 10^{-23} J K^{-1}); T (K) is the absolute temperature; μ (kg m^{-1} s^{-1}) is the absolute viscosity of the fluid (water). The van der Waals number N_{vdW} is defined as:

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

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

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

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

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}.

4. Consolidated core transport breakthrough curve:

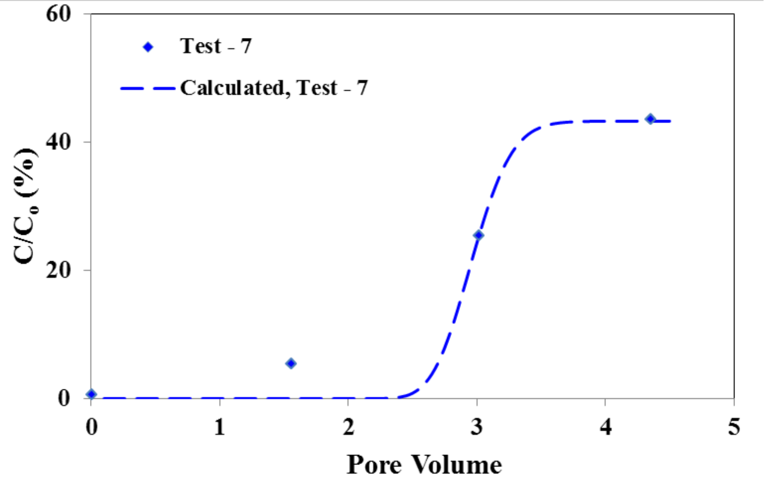

Figure ESI-1 Breakthrough curve of SINC particles in consolidated sandstone core (TE #7). Diamond dots were experimentally obtained and the dashed line was obtained from advection dispersive equation calculation.

References:

1. R.K. Rana, V.S. Murthy, J. Yu and M.S. Wong, Nanoparticle Self-Assembly of Hierarchically Ordered Microcapsule Structures, Adv. Mater., 2005, 17, 1145-1150.
2. J. Yu, V.S. Murthy, R.K. Rana and M.S. Wong, Synthesis of nanoparticle-assembled tin oxide/polymer microcapsules, Chem. Commun., 2006, 1097–1099.
3. J. Yu, M.A. Yaseen, B. Anvari and M.S. Wong, Synthesis of Near-Infrared-Absorbing Nanoparticle-Assembled Capsules, Chem. Mater. 2007, 19, 1277-1284.
4. R. J. Charbeneau, Groundwater Hydraulics And Pollutant Transport, 1st edn, Waveland Press, Long Grove, IL, 2006.
5. M.M. Clark, Transport Modeling for Environmental Engineers and Scientists, 2nd edn., John Wiley & Sons, Hoboken, NJ, 2009.
6. J.N. Ryan and M. Elimelech, Colloid mobilization and transport in groundwater. Colloids Surf., A, 1996, 107, 1-56.
7. Parker, J. C. and van Genuchten, M. T., Determining Transport Parameters from Laboratory and Field Tracer Experiments. Blacksburg, VA, 1984; Vol. Bulletin 84-3.
8. N. Tufenkji and M. Elimelech, Correlation Equation for Predicting Single-Collector Efficiency in Physicochemical Filtration in Saturated Porous Media. Environ. Sci. Technol. 2004, 38, 529-536.