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In Situ Measurement and Simulation of Nano-Magnetite Mobility in Porous Media Subject to Transient Salinity

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Abstract

Nanotechnologies have been proposed for a variety of environmental applications, including subsurface characterization, enhanced oil recovery, and in situ contaminant remediation. For such applications, quantitative predictive models will be of great utility for system design and implementation. Electrolyte chemistry, which can vary substantially within subsurface pore waters, has been shown to strongly influence nanoparticle aggregation and deposition in porous media. Thus, it is essential that mathematical models be capable of tracking changes in electrolyte chemistry and predicting its influence on nanoparticle mobility. In this work, a modified version of a multi-dimensional multispecies transport simulator (SEAWAT) was employed to model nanoparticle transport under transient electrolyte conditions. The modeling effort was supported by experimental measurements of paramagnetic magnetite (Fe3O4) nanoparticle, coated with polyacrylamide-methylpropane sulfonyl acid – lauryl acrylate (nMag-PAMPS), mobility in columns packed with 40-50 mesh Ottawa sand. Column effluent analyses and magnetic resonance imaging (MRI) were used to quantify nanoparticle breakthrough and in situ aqueous phase concentrations, respectively. Experimental observations revealed that introduction of de-ionized water into the brine saturated column (80 g/L NaCl + 20 g/L CaCl2) promoted release and remobilization of deposited nanoparticles along a diagonal front, coincident with the variable density flow field. This behavior was accurately captured by the simulation results, which indicated that a two-site deposition-release model provided the best fit to experimental observations, suggesting that heterogeneous nanoparticle-surface interactions governed nanoparticle attachment. These findings illustrate the importance of accounting for both physical and chemical processes associated with changes in electrolyte chemistry when predicting nanoparticle transport behavior in subsurface formations.
1. Introduction

Engineered nanomaterials are currently being evaluated for their potential to improve subsurface applications including oil reservoir characterization,\textsuperscript{1-4} carbon sequestration,\textsuperscript{5-8} enhanced oil recovery,\textsuperscript{5-8} and groundwater remediation.\textsuperscript{9,10} The proposed applications rely on the ability to engineer nanoparticles to perform certain tasks within the subsurface environment, including transport to a targeted zone, association with a specific interface, and/or completion of a specific activity or process at that interface.\textsuperscript{10} However, performance of these functions is strongly dependent upon particle-particle and particle-surface interaction energies, and as a consequence, the chemistry of the pore water (e.g., ionic strength, pH, concentration of surface-active agents).\textsuperscript{10-13} Since nanoparticle mobility in the subsurface will be a critical process in these applications, the ability to accurately simulate the effects of transient aqueous chemistry on nanoparticle transport behavior is essential for proper delivery system design and deployment (or implementation).

Prior studies have demonstrated that the electrolyte chemistry of nanoparticle suspensions strongly influences their aggregation and deposition potential in porous media.\textsuperscript{14} An increase in ionic strength acts to suppress the electrical double layer surrounding a nanoparticle, which decreases the electrostatic repulsion between the nanoparticle and the solid phase surfaces.\textsuperscript{15} The response to such a change in solution chemistry is often reflected in macroscale nanoparticle transport behavior, where increasing ionic strength promotes particle-particle aggregation and particle deposition.\textsuperscript{16} These effects have been reported for a variety of nanoparticle types, including fullerenes,\textsuperscript{17} iron,\textsuperscript{18,19} titanium dioxide,\textsuperscript{20-23} silver,\textsuperscript{24} quantum dots,\textsuperscript{25} and others.\textsuperscript{26-28} Adding to this complexity, nanoparticles that are introduced into a subsurface formation will be exposed to a variety of dissolved compounds in the interstitial pore water. For example, the
presence of divalent cations may also promote aggregation and deposition by bridging
complexation,\textsuperscript{24,29,30} which could lead to variable interaction energies between particles and
surfaces. Despite these potential complexities, most nanoparticle transport studies conducted to
date consider nanoparticle deposition to the solid phase as a single-site process and neglect the
heterogeneous interaction energies that could be experienced by nanoparticles in natural porous
media.

Many subsurface formations can experience transient salinity conditions that lead to altered fluid flow behavior.\textsuperscript{31} For example, nanotechnologies have been proposed for use in oil reservoir characterization and enhanced oil recovery.\textsuperscript{2,5,7,32,33} A fundamental challenge in these applications is the effect of the high salinity reservoir environment (>1 M) on nanoparticle suspension stability.\textsuperscript{34} While a number of experimental investigations have focused on increasing nanoparticle suspension stability in such harsh pore waters,\textsuperscript{34-36} studies have yet to evaluate the coupled effects of transient electrolyte conditions on variable density fluid flow and nanoparticle transport in the subsurface.

Most macroscale mathematical models designed to simulate nanoparticle transport in porous media employ modifications of clean-bed colloid filtration theory.\textsuperscript{37} For example, a modified filtration theory (MFT) model, which incorporates a limiting retention capacity term (\(S_{\text{max}}\)), has been successfully used to simulate nanoparticle attachment behavior in a range of soils and aquifer materials, including those subject to transient solution chemistry.\textsuperscript{38-42} The deposition behavior of nanoparticles, however, is much better understood than nanoparticle release, in part because irreversible attachment (\textit{i.e.}, no observable detachment) is typically observed under relevant environmental conditions, especially in systems containing divalent cations.\textsuperscript{29,43} In addition, nanoparticle detachment and re-entrainment in flowing pore water (\textit{i.e.},
release) may strongly depend on transient hydrodynamic and thermodynamic system characteristics,\textsuperscript{44,45} and may alter the retention capacity of the system.\textsuperscript{46} A few studies have modeled reversible attachment by identifying a releasable fraction of nanoparticles, a system-specific parameter related to the interaction energies between particles and surfaces.\textsuperscript{29,38,47}

Although these models provide useful information regarding the relative populations of releasable and non-releasable particles in a particular system, they only account for variability in the detachment process, not in the attachment process. In addition, these studies only considered relatively minor variations in ionic strength in freshwater aquifer formations, and thus, do not account for the potential effects of solution density contrasts on flow in estuarine aquifers or oil reservoirs. To our knowledge, no mathematical modeling studies have addressed the coupled influence of transient electrolyte chemistry on nanoparticle attachment-detachment kinetics and flow behavior.

The objective of this study was to quantify the coupled physical and chemical effects created by a transient salinity environment on the release behavior of polymer-coated magnetite nanoparticles (nMag) in water-saturated quartz sand. Two column studies were performed; the first was designed to measure the effluent concentration of nMag during transport and release, while the second was designed to obtain \textit{in situ} images of nMag transport behavior using magnetic resonance imaging (MRI).\textsuperscript{48} The initial phases of the nMag transport studies were performed under brine conditions, followed by the introduction of de-ionized (DI) water to explore the release of deposited nanoparticles. The coupled effects of variable density flow and transient ionic strength on nMag release were modeled by modifying an existing variable density groundwater flow simulator to include nMag transport, deposition, and fractional release using
an MFT-based approach. To quantify the deposition and release kinetics observed in the column experiments, the model was fit to column effluent data, and further validated using MRI results.

2. Experimental Methods

2.1 Column Experiments: Magnetite nanoparticles (nMag, $\text{Fe}_3\text{O}_4$), coated with polyacrylamido-methylpropane sulfonic acid-lauryl acrylate (nMag-PAMPS), were utilized in this study based on their propensity to remain stable at high salinity. Details of the synthesis of these particles are presented by Colvin and Zhu. Two replicate column experiments were conducted following methods described in previous studies. Briefly, for both nanoparticle transport experiments (nMag-eff and nMag-MRI), borosilicate glass columns (2.5 cm i.d. × 10 cm length) were dry packed with 40-50 mesh Ottawa sand (U.S. Silica, Berkeley Springs, WV). To ensure complete saturation, the packed columns were purged with CO$_2$ gas and flushed with at least 10 pore volumes (PVs) of American Petroleum Institute (API) brine solution (8 wt% NaCl, 80 g/L and 2 wt% CaCl2) at pH 7, designed to mimic oil reservoir salinity. A pulse (ca. 1.3 PVs) of aqueous nMag suspension (30 mg/L as Fe) was introduced into the brine-saturated column (pH 7), followed by 1.5 PVs of nMag-free brine solution. To investigate the release of attached nMag-PAMPS, the column was then flushed with DI water for 2.6 PV. Due to restricted orientation of the MRI device, the column studies were performed using a horizontal orientation (i.e., flow perpendicular to gravity) at a flow rate of 0.4 mL/min (Darcy velocity of ca. 1.0 m/d). In the first column experiment (nMag-eff), effluent samples were collected continuously to produce an effluent breakthrough curve, represented as the relative effluent concentration versus the number of dimensionless pore volumes injected. In the second column experiment (nMag-MRI), the entire column was located within the MRI device, allowing for the collection of in situ images of the flow field following the methods described below. Although the two nMag column
experiments were conducted under identical conditions, effluent samples were not collected
during the nMag-MRI experiment because of physical restrictions imposed by the magnet.

The magnetic imaging device consisted of a wide-bore static field 2T (1H 85 MHz) magnet
(Nalorac Cryogenics, Walnut Creek, CA), a Bruker Biospec spectrometer console (Bruker
BioSpin, Billerica, MA), and a ParaVision acquisition platform. Prior to use, the MRI system
was calibrated using a CuSO$_4$–doped agar. The brine-saturated column was placed into a radio
frequency (RF) probe (i.d. = 125 mm) consisting of a birdcage coil tuned to 85 MHz with both
cylindrical axes aligned. The probe was placed horizontally in the center homogeneous region of
the magnet. Following calibration and setup of the MRI system, the nMag-MRI column was run
according to the procedures outlined above. Sagittal (i.e., side view) and axial (i.e., cross-
sectional view) magnetic resonance profiles of the spin-spin relaxation time ($T_2$) and relaxation
rate ($R_2 = 1/T_2$) were obtained every 3.5 min using a multiple slice multiple echo (MSME)
imaging experiment$^{50}$ with an in-plane resolution of 0.98 mm and slice thickness of 2 mm with
an echo time $TE = 13$ ms and a repetition time $TR = 1.5$ s. MSME can yield the equivalent
NMR signal decay data as the Carr-Purcell-Meiboom-Gill (CPMG) pulse-echo sequence,$^{33,51}$ but
with spatial resolution. A diagram of the column orientation within the MRI device and the
resulting image orientations are presented in Figure S1.

2.2 Analytical Methods: The mean hydrodynamic diameter of the nanoparticles was determined
by dynamic light scattering (DLS) using a Zetasizer Nano ZS Analyzer (Malvern Instruments,
Southborough, MA), operated in non-invasive back scattering (NIBS®) mode at an angle of 173°.
To determine nMag-PAMPS concentrations in aqueous samples, elemental Fe present in the
nanoparticles was quantified using an Optima 7300 DV inductively coupled plasma – optical
emission spectrometer (ICP-OES; Shelton, CT) based upon a five-point calibration curve
obtained over a concentration range of 0.5 to 50 mg Fe/L. Solid-phase samples were collected near the column inlet and prepared for scanning electron microscopy (SEM) imaging by attaching sands grain onto an aluminum mount stub (Electron Microscopy Sciences) covered with conductive carbon tape (Electron Microscopy Sciences). The samples were then air-dried overnight and analyzed using a Zeiss Ultra Plus field emission SEM (Carl Zeiss Microscopy, LLC, Peabody, MA) with charge compensation operated at 3 kV.

3. Mathematical Model Development

3.1 Coupled Flow and Transport Model: The horizontal orientation of the experimental column, required by the MRI apparatus (see Materials and Methods), coupled with the application of transient brine chemistry floods, created non-uniform, variable density, flow conditions. To simulate this flow behavior, a variable density aqueous phase flow equation was employed:

\[
\nabla \cdot \left[ \rho \frac{\mu}{\mu_0} K_0 \left( \nabla h + \frac{\rho - \rho_0}{\rho_0} \nabla z \right) \right] = \rho S_{s,0} \frac{\partial h_0}{\partial t} + \theta_w \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} - \rho_s q_s \quad (1)
\]

where \( S_{s,0} \) is the specific storage coefficient of the porous medium \([L^{-1}]\), \( h_0 \) is the potentiometric head of the reference fluid (de-ionized water) \([L]\), \( K_0 \) is the hydraulic conductivity tensor \([L \cdot T^{-1}]\), \( \rho \) is fluid density \([M \cdot L^{-3}]\), \( \mu \) is fluid viscosity \([M \cdot T^{-1} \cdot L^{-1}]\), \( \rho_0 \) and \( \mu_0 \) are a reference density and viscosity, respectively, at which fluid and aquifer properties are known, \( \theta_w \) is the volumetric water content \([-]\), \( h \) is pressure head \([L]\), \( z \) is elevation head \([L]\), and \( \rho_s q_s \) is a volumetric flux source term \([M \cdot L^{-3} \cdot T^{-1}]\) with \( \rho_s \) being the density of the source fluid. Note that for constant density, this equation reduces to the traditional groundwater flow equation. To track the
influence of brine concentration on fluid density, the spatiotemporal brine concentration profile was resolved using a traditional component mass balance equation:

\[
\frac{\partial (\theta_w C_i)}{\partial t} = \nabla \cdot (\theta D_i \nabla C_i) - \nabla \cdot (\theta_w v_p C_i) + q_s C_{i,s} + \sum R_n
\]  

(2)

Here \(C_i\) is the aqueous concentration of constituent \(i\) [M L\(^{-3}\)], \(D_i\) is the hydrodynamic dispersion tensor for constituent \(i\) [L T\(^{-2}\)], \(v_p\) is the pore-water velocity [L T\(^{-1}\)], \(q_s\) is a volumetric flow rate per unit volume of aquifer representing sources and/or sinks which include constituent \(i\) [T\(^{-1}\)], \(C_{i,s}\) is the concentration of the source/sink fluid, and \(R_n\) is the \(n\)-th reaction which transforms constituent \(i\). In the case of brine transport, the cation exchange capacity of the sand was considered negligible, such that \(R_n = 0\).

A linearized equation of state (3) was then used to represent density, incorporating a volumetric expansion coefficient, \(\beta_c\), for salt concentration (4):

\[
\rho = \rho_0 \exp[\beta_c (C - C_0)] \approx \rho_0 + \rho_0 \beta_c (C - C_0)
\]  

(3)

\[
\beta_c = \frac{1}{\rho_0} \left( \frac{\partial \rho}{\partial C} \right)_{T,P}
\]  

(4)

Solution of equations (1) through (4) was implemented using the SEAWAT version 4 software package, an open-source groundwater flow and transport code developed by the USGS.\(^{52}\)

SEAWAT is a modification of the MODFLOW-MT3DMS suite\(^{54,55}\) which is often used to simulate variable density groundwater flow and transport due to transient concentration (i.e. salt), heat, or pressure, especially in estuarial environments.\(^{56,57}\) The SEAWAT simulator offers the ability to account for multiple constituents simultaneously, a feature which was utilized in this study to examine the influence of transient brine concentration on nanoparticle attachment and detachment behavior. Note that, in this scenario, it was assumed that the dilute...
concentrations of nMag (< 30 mg/L) would have a negligible influence on the fluid density (<0.01%).

3.2 Nanoparticle Deposition and Release Models: Nanoparticle transport was calculated using a balance equation of the form (2), with $R_n$ representing the interaction between nanoparticles and the solid surface. To accommodate two types of deposition sites on the solid surface, strongly-held non-releasable (e.g., in the primary energy minimum) and weakly-held releasable (e.g., in the secondary energy minimum) sites, utilization of a commonly employed two-site filtration model is proposed:

$$\rho_b \frac{\partial S^n}{\partial t} = \rho_b \frac{\partial S^n}{\partial t} + \frac{\partial S^n_{nr}}{\partial t} = \theta_w k_{att,r} \Psi_r C^n + \theta_w k_{att,nr} \Psi_{nr} C^n - \rho_b k_{det,r} S^n$$

(5)

$$\Psi_r = \frac{s_{max,r} - s^n}{s_{max,r}}$$

$$s_{max,r} = f_r * S_{max}$$

(6)

$$\Psi_{nr} = \frac{s_{max,nr} - s_{nr}^i}{s_{max,nr}}$$

$$s_{max,nr} = (1 - f_r) * S_{max}$$

(7)

where the $r$ and $nr$ subscripts represent releasable and non-releasable sites, respectively, $k_{att}$ is the attachment rate of nanoparticle constituent $i$ [$T^{-1}$], $S^i$ is the attached phase concentration of constituent $i$ [M/M], $k_{det,r}$ is the detachment rate of attached phase nanoparticles from releasable sites [$T^{-1}$], and $\Psi_r$ and $\Psi_{nr}$ are Langmuir-type blocking functions for each site type, described by (6) and (7). The fraction of releasable sites ($f_r$) divides the total retention capacity into separate capacities for releasable and non-releasable sites, $S_{max,r}$ and $S_{max,nr}$, respectively. This model is similar to that presented in Bradford et al.$^{29, 47}$ in that the releasable particles are treated separately from non-releasable particles through implementation of a fraction. Herein, the two sites are considered separate throughout the entire experiment, rather than only during the release phase, similar to the approach of Tosco et al.$^{38}$ Consistent with other MFT-based models, as the concentration of attached phase particles approaches the maximum retention capacity of a site
type, $\Psi$ decreases from unity, effectively slowing down, and eventually eliminating, the kinetic attachment of suspended nanoparticles to those sites.

The detachment rate for releasable sites is assumed to be a step function of the aqueous salt concentration:

$$k^n_{\text{det},r} = k^n_{\text{det},r}(C^\text{brine}) = \begin{cases} k^n_{\text{det}} & \text{if } C^\text{brine} \leq CRC \\ 0 & \text{if } C^\text{brine} > CRC \end{cases}$$

where $C^\text{brine}$ is the concentration of brine in a given volume, $CRC$ is the critical release concentration of brine, and $k^n_{\text{det}}$ is the detachment rate for particles in regions in which the brine concentration is below the critical release concentration. This model is similar to the Heaviside model proposed by Bradford et al., but allows the user to include the $CRC$ specific to the system of interest.

### 3.3. Mathematical Model Implementation:

Implementation of the mathematical model in the SEAWAT framework was accomplished by adapting the non-equilibrium sorption reaction module in MT3DMS:

$$R_n = \beta \left( C^i - \frac{S^i}{K_d} \right)$$

where $\beta$ and $K_d$ are non-equilibrium sorption parameters required by MT3DMS. For nanoparticle attachment and release, the following functional forms were implemented for $\beta$ and $K_d$:

$$\beta = \theta_w k^n_{\text{att}} \Psi \quad K_d = \frac{\theta_w k^n_{\text{att}} \Psi}{\rho_k k^n_{\text{det}}}$$

The code was modified to update these terms in space and time according to changes in attached nanoparticle mass. The two-site model described in equations (5)-(8) was implemented using two separate $R_n$ terms, one for each class of attachment sites, $r$ and $nr$. It should be noted that in
this implementation, $k_{det}$ resides in the denominator of the $K_d$ coefficient, which requires that $k_{det}$ be set to $\varepsilon = 1 \times 10^{-10}$ when the model defines it to be zero.

The column was simulated as a three dimensional rectangular prism, with the cross sectional area equivalent to that of the experimental column (Figure S1). This simplified configuration was used to reduce computational time and provided only negligible differences from simulation results using a circular cross section. All outer boundaries were treated as no-flow boundaries. Influent/effluent ports were simulated by implementing a MODFLOW (injection/extraction) well boundary condition at the center node in the first and last column cross sections. The column inlet screen, which is designed to contain the porous media within the column, also allows for influent fluid to spread across the column cross section. To mimic this behavior in the model, the hydraulic conductivity of the first cross section of cells was set at a value $10^3$ times greater than the hydraulic conductivity of the 40-50 mesh sand.

3.4 Model Parameter Estimation: Hydrodynamic dispersion for the 40-50 mesh Ottawa sand used in this study was estimated from non-reactive tracer tests in similar experiments from a previous study to be $1.39 \times 10^{-2}$ cm²/min. All parameter estimation for nanoparticle attachment and detachment was conducted using a non-linear least squares optimization algorithm provided by MATLAB (The Mathworks, Natick, MA).

4. Results and Discussion

4.1 nMag Column Result: Effluent breakthrough data for the transport of nMag-PAMPS through Ottawa sand are presented in Figure 1 (experiment nMag-eff). Here, Phases 1, 2, and 3 represent the periods of 30 mg/L nMag suspension injection into the brine-saturated column, the nMag-free brine flush of the column, and the injection of DI water through the column,
respectively. At the applied pore-water velocity of 3.1 m/d, nMag-PAMPS exhibited slightly
delayed breakthrough (ca. 1.3 PVs). Once breakthrough occurred, nMag-PAMPS reached a
maximum effluent concentration of 24 mg nMag/L ($C/C_0 = 0.78$) at 2.1 PV. Following the pulse
injection, the nMag-PAMPS concentration decreased rapidly, with approximately 46% of the
applied mass (ca. 918 ug) recovered in the column effluent (ca. 54% retained). Detachment
(release) of deposited nMag-PAMPS occurred following the introduction of DI water, with
measurable nMag-PAMPS concentrations in the column detected approximately 1.0 PV after
initiation of the DI water flood. Introduction of 2.4 PVs of DI water resulted in the release of
approximately 21% of retained nanoparticle mass, leaving approximately 43% of the total
injected mass retained at the conclusion of the column experiment. In the replicate column
experiment, the nMag hydrodynamic diameter was measured in the influent chamber and
periodically in the effluent (Figure 1A). During phases 1 and 2, nMag size remained relatively
constant, with an average effluent hydrodynamic diameter of 56 nm, compared to 52 nm in the
influent. During phase 3, however, eluted nMag particles exhibited an average hydrodynamic
diameter of 97 nm, suggesting that released nMag particles had a greater propensity for
aggregation after re-entrainment or were deposited on the surface as agglomerates.

Representative SEM images of nMag deposited on 40-50 mesh Ottawa sand (Figure 2) reveal
that nMag attachment resulted in limited coverage of the sand surface, even at high loading (3.1
pore volumes at 1,000 mg Fe/L), and did not approach monolayer coverage. These observations
are consistent with the results of prior nanoparticle transport studies$^{38-41}$ and further support the
concept of a limited or maximum nanoparticle retention capacity (Equations 5-7). In addition,
calculated traditional and extended DLVO interaction energy profiles suggested that steric
repulsion provided only a weak attractive force between nMag and the sand surface, a result
which was consistent with the small amount of retention observed (Figure S4).

In the second column experiment (nMag-MRI), the spin-spin relaxation time ($T_2$), or
equivalently the relaxation rate, $R_2 = 1/T_2$, of the bulk fluid was measured periodically along
sagittal and axial planes of the column using the MRI device (Figure 3). Iron nanoparticles have
long been demonstrated to induce a strong shift in $T_2$, even at low concentrations and under weak
magnetic fields, making them ideal contrast agents for a variety of applications. As a
relaxation rate, this shift is additive with respect to other contributions and proportional to
particle concentration for a fixed particle type and aggregation state, e.g. $R_2 = R_{2,\text{bulk}} +
\kappa C_{n\text{Mag}}$, where $R_{2,\text{bulk}}$ represents the relaxation rate of the bulk fluid in the absence of nMag
particles, and $\kappa$ represents the relaxivity, a proportionality constant which is sensitive to particle
aggregation state. Thus, under stable aggregation conditions, magnetic nanoparticle
concentrations can be quantified because they are linearly correlated to $R_2$. Furthermore, under
our experimental configuration, only pore-water suspended nMag particles are detected as
confirmed by the imaging measurements. Surface adhered nMag particles typically produce a
substantially smaller effect, because individual particles can only affect the signal from bulk
fluid molecules that diffuse within a region on the order of their size and surface adhesion
reduces this effective volume.

In Figure 3, the strong signal (red) indicates high $R_2$, consistent with the presence of
suspended nMag nanoparticles in the pore water, while the weak signal (blue) indicates a low $R_2$
consistent with nMag-free brine solution. $R_2$ was linearly correlated to the suspended nMag
concentration in the pore water under constant brine conditions (Figure S2):
Previous studies have also demonstrated that the $R_2$ is strongly sensitive to nanoparticle aggregate size and geometry:\textsuperscript{32, 33, 51, 61}

\[ R_2 \propto \left( \frac{n}{r_G^3} \right)^2 r_G^2 \]

where $r_G$ is the radius of gyration of the aggregate and $n$ is the number of primary particles in the aggregate. Because of this non-linear dependence of $R_2$ on nMag particle size, quantification of nMag concentration from $R_2$ data was only possible during Phases 1 and 2 of this experiment (Figure 1). Thus, $R_2$ profiles were primarily used to indicate presence and location of suspended nMag particles during Phase 3.

During phase 1, nMag-PAMPS were uniformly distributed in the aqueous phase after the introduction of 1.36-PVs of the influent suspension which contained ca. 30 mg/L as Fe nMag-PAMPS in brine (density ca. 1.07 g/mL) (Figure 3, panels A-D). The nMag-free brine flush, which was initiated in Phase 2 of the experiment, displaced suspended nMag particles from the column (Figure 3, panels E-G). As noted previously, the MRI configuration did not detect attached particles, and thus, the column appears completely dark blue at the conclusion of Phase 2 (Figure 3, panel G). At this stage of the experiment, approximately 46% of the applied nMag was eluted from the column and the remaining 54% of the applied mass was deposited on the quartz sand. To evaluate the release of deposited nMag, the column was then flushed with DI water (Phase 3, Figure 3, panels H-I). Due the density contrast between the resident brine solution ($\rho_l$ ca. 1.07 g/mL) and the injected DI water ($\rho_l$ ca. 0.997 g/mL), a diagonal fluid density front formed within the column, resulting in flow override of lower-density DI water above the more dense resident brine solution. Along this density contrast front, a strong increase in $R_2$
developed, indicating detachment and re-entrainment of nMag-PAMPS in the pore fluid (Figure 3, panels H-I). This behavior was attributed to the reduction in pore-water ionic strength due to the DI water flood, which resulted in lower nMag-sand surface attractive forces and subsequent nMag detachment. The shift in $R_2$ was negligible up-gradient from the angled nMag release front, indicating that nMag remaining at that location within the column was still strongly attached to the solid surface. In response to the DI water flood, approximately 11% of the applied nMag mass was released from sand surfaces, while 43% of the applied nMag remained attached. The fraction of deposited nMag mass that remained attached (ca. 80% of the total deposited mass) was considered to be irreversibly attached under these experimental conditions. These particles may have been strongly retained on the sand surface due to calcium ion bridging across the primary energy barrier.\textsuperscript{17, 24, 42} In order to account for the different populations of attached particles (\textit{i.e.}, releasable and non-releasable), a two-site detachment model\textsuperscript{29} was employed to capture the nanoparticle release behavior observed in Phase 3. The results of nMag-eff and nMag-MRI column experiments clearly demonstrate the influence of ionic strength and fluid density on nanoparticle transport, retention, and release under these experimental conditions.

4.2 Modeling nMag Injection and Deposition: Detachment of deposited nMag mass was eligible during Phases 1 and 2 of the column experiments, as supported by the minimal $R_2$ signal observed within the column following the passage of the nMag pulse (Figure 3), combined with the absence of tailing in the effluent breakthrough curve prior to introduction of DI water (Figure 2A). A relatively sharp vertical displacement front was observed during Phases 1 and 2 of the nMag-MRI column experiment (Figure 3) because the 30 mg/L nMag brine suspension was injected into a brine-saturated column which had a similar fluid density. Based on these
observations, a traditional one-dimensional version of the model presented in equations (2), (5), and (6) was used to determine the nMag attachment parameters.\textsuperscript{39-41} Attachment to the releasable and non-releasable sites was assumed to occur at the same rate. Based on this assumption, $k_{\text{att},r}$ and $k_{\text{att},nr}$ were approximated as a single attachment rate, $k_{\text{att}}$; likewise, $S_{\text{max},r}$ and $S_{\text{max},nr}$ were combined into a single site, represented by the total retention capacity, $S_{\text{max}} = S_{\text{max},r} + S_{\text{max},nr}$.

The fitted nMag breakthrough curve for Phases 1 and 2 ($k_{\text{att}}=5.28 \text{ hr}^{-1}$ and $S_{\text{max}}=5.42 \text{ ug/g}$) is plotted with the experimental data in Figure 1A. The MFT model successfully captured the nMag transport behavior, including the delayed breakthrough time (ca. 1.3 PV) and magnitude, as well as the absence of breakthrough curve tailing following the passage of the nMag pulse. The model-predicted solid phase retention profile following the conclusion of Phase 2 is shown in Figure 1B, and indicates that the available nMag retention sites were completely saturated near the column inlet, decreasing to 97% site saturation near the column outlet. This retention behavior is consistent with the experimental breakthrough curve, which reached a maximum relative concentration ($C/C_0$) of 0.8, indicating that additional solid phase retention sites were still available in the column. Based on the ability of the model to capture all aspects of the breakthrough curve, the assumption of a single-site attachment model was considered to be appropriate for Phases 1 and 2 of the experiment. The fitted $k_{\text{att}}$ and $S_{\text{max}}$ were then used in the multi-dimensional nanoparticle release model to simulate the entire nMag column experiment (i.e., Phases 1-3) discussed below.

\textbf{4.3 Modeling nMag Release:} In the MRI imaging results (Figure 3), the angled front observed in Phase 3 was associated with both density driven flow and nanoparticle detachment, each resulting from the transient brine conditions within the column. To appropriately model this
behavior, it was necessary to couple three-dimensional simulation of transient flow with ionic
strength induced nanoparticle detachment through the modified SEAWAT code. Since nMag
detachment behavior depends simultaneously on flow and chemistry in the experiment,
independent experimental determination of the detachment parameters specified in (5)-(7), $k_{det}$
and $f_r$, was not possible. Thus, the modified SEAWAT model was fit to Phase 3 of the measured
effluent breakthrough curve (Figure 1). The model results were then compared to the observed
$R_2$ profiles at consistent time points to ensure that the simulation appropriately captured the
observed variable density flow behavior (Figure 4).

Figure 4A presents the simulated centerline sagittal plane salt concentration profiles,
which are independent of the nanoparticle transport behavior. Comparing Figure 4A with
Figures 3H and 3I, it is apparent that the nMag re-entrainment front occurs along the same angle
as the salt concentration contours in that plane. This behavior is consistent with the hypothesis
that nMag detachment occurred in response to the reduction in ionic strength resulting from DI
water front. The nanoparticle release front was observed to occur at approximately the 45 g/L
salt concentration contour, and thus the critical release concentration ($CRC$) in subsequent
modeling was specified as 45 g/L.

Using a $CRC$ value of 45 g/L, the two-site model (equations (5)-(7)) was fit to the Phase
3 effluent data (3.0 – 5.4 PV) from the nMag-eff column experiment, where $f_r$ and $k_{det}$ were the
only fitted parameters. The two-site detachment model successfully captured the measured
effluent concentrations from Phase 3, including the timing of the peak nMag release (ca. 4.0 PV)
and the slope of the subsequent tailing (Figure 1A). The predicted final nMag retention profile
(Figure 1B) was flat, at a constant value of 3.25 ug/g. Given that the fitted fraction of detachable
mass was 0.40, a comparison of the retained mass with the $S_{max}$ value of 5.42 ug/g indicates that
nearly all (> 99%) of the detachable mass had been released by the end of the simulation. The fitted detachment rate, $k_{det}$, was 2.76 hr\(^{-1}\), a slightly slower rate than that of attachment ($k_{att}$ = 5.29 hr\(^{-1}\)). Measured retention profiles were not available for these experiments due to the inability to accurately distinguish between nMag associated iron and sand-associated iron in digested solid-phase samples. However, nMag effluent concentrations at the end of the experiment decreased to below $C/C_0 = 0.05$, indicating that the detachment process was essentially complete.

Integration of the experimental and model breakthrough curves showed that the model was able to accurately capture the quantity of mass released in Phase 3, (94.1 ug simulated with 94.3 ug measured). Simulation of the nMag suspended concentration profile indicated that some suspended mass was still remaining in the column at the end of the simulation, mass which explains the continuation of the downward slope at the end of the breakthrough curve.

Furthermore, although the two-site model was not able to be fit to phases 1 and 2 of the experiment due to the absence of retention data, two-site model predictions of these phases using parameters fitted in phase 3 suggested that the one-site model provided a reasonable estimation of the retention capacity of the system (See Figure S3).

Comparison of sagittal $R_2$ profiles (Figure 3) and simulated nMag concentration profiles (Figure 4) indicates that the variable density two-site detachment model was able to capture the nanoparticle release behavior observed in the nMag-MRI experiment. The two-site detachment model successfully captured the narrow band of nMag released along the angled injected and resident fluid front as seen in the $R_2$ profiles. Additionally, the model was able to capture the decreasing angle of the nMag front as it passed through the column. This finding suggests that the angled release behavior was primarily due to the non-uniform flow patterns created by the density contrast at the DI water-brine mixing front.
4.4 Comparison of Nanoparticle Release Models: To further explore the difference between the two-site detachment model utilized here and more traditional one-site attachment models, an additional simulation was performed. In this simulation $f_2$ was set to 1 so that the model reduced to a traditional MFT model with detachment. This resulted in a one parameter model fit to the detachment rate, $k_{det}$, obtained using the same fitting procedure that was employed for the two-site model simulations. Comparison of the model fit to the measured effluent breakthrough curve (Figure 1A) showed that the one-site model was able to capture the concentration of nMag mass observed in the column effluent at the end of the experiment (ca. 5.4 PV), but was unable to reproduce the concentration peak at 4.0 PV and the downward slope from 4.0 to 5.4 PV.

Comparison of the simulated concentration profiles (Figure 4C) to those for the two-site model (Figure 4B) and the $R_2$ profiles (Figure 3) demonstrate that the one-site model was unable to capture the absence of nMag remobilization upstream of the initial front seen in the nMag-MRI experiment, despite successfully simulating the decreasing angle of the concentration front. At the end of the one-site model simulation, nMag detachment continued, a result that is not consistent with both the MRI results and the effluent results. The inability of the one-site model to capture the behavior observed during Phase 3 further supports the use of a two-site model to describe nMag release and re-entrainment in the pore fluid.

5. Conclusions

To our knowledge, this work presents the first validated mathematical model that couples nanoparticle transport, deposition, and release using a variable density flow simulator. The influence of transient ionic strength on nanoparticle interaction energies of aggregation and deposition has been well studied and modeled, yet prior studies have not included the
potential effects of ionic strength (i.e., density contrast) on simultaneous fluid flow. These processes should be accounted for in systems where changes in salt or background electrolyte levels are sufficient to induce nanoparticle detachment and re-entrainment in the mobile phase, and when flow is altered as a result of density gradients. Relevant scenarios include the use of nanoscale contrast agents for down-hole reservoir characterization, where pore-water salinity may differ from that of the injected water, and nanomaterial fate and transport aquifer formations that are subject to salt water intrusion.

Acknowledgements

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Electronic Supplementary Information (ESI): A schematic diagram of the nMag-MRI experimental systems, description of the mathematical modeling domain, further information regarding calibration of $R_2$ to nMag concentration in sand, comparison of one- and two-site
simulations of phases 1 and 2, DLVO interaction energy profiles for the system, and a time lapse movie of the best fit two-site model simulation of the nMag experimental data.
References

Table 1. Experimental and model parameters for the column experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>( D^a )</td>
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<tr>
<td>( L^b )</td>
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<td>( C_0 – Salt^l )</td>
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<tr>
<td>( \rho_{Brine}^p )</td>
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Superscripts: 
- \(^a\) – column diameter; \(^b\) – column length; \(^c\) – mean sand grain size; \(^d\) – volumetric water content; \(^e\) – Flow rate; \(^f\) – pore water velocity; \(^g\) – hydrodynamic dispersion; \(^h\), \(^i\), \(^j\) – pulse widths for each phase; \(^k\), \(^l\) – initial concentrations for each constituent; \(^m\) – percent retention; \(^n\) – DI water density; \(^p\) – Brine density.

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
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<tr>
<td>( k_{att,c}^c )</td>
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<td>( S_{max}^d )</td>
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</tr>
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<tr>
<td>CRC</td>
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Superscripts: 
- \(^a\) – Volumetric expansion coefficient for salt concentration; \(^b\) – attachment rate for non-releasable sites; \(^c\) – attachment rate for releasable sites; \(^d\) – total solid phase retention capacity; \(^e\) – fraction of releasable sites; \(^f\) – detachment rate for releasable sites.
**Fig. 1:** Effluent nMag breakthrough curves and simulated retention profiles. On the breakthrough curve, simulation results are shown from the 1D model for phases 1 and 2 and from the multi-dimensional model for phase 3. Breakthrough results in phase 3 are from the one- and two-site release models. On the retention curve, predicted retention profiles are shown at the end of phase 2, and the end of phase 3 for one- and two-site release models.
**Fig. 2:** SEM Images of nMag nanoparticles deposited on the surface of 40-50 mesh Ottawa Sand from a representative column experiment following a 3.1 PV injection of 1000 mg/L nMag suspension.
**Fig. 3**: Time series of measured relaxation rate ($R_2$) along the sagittal plane of the imaged column. The first column presents the nMag injection phase (Phase 1), the second presents the brine flush phase (Phase 2), and the third presents the DI flush phase (Phase 3). Horizontal and vertical axes correspond to length in millimeters.
Fig. 4: Comparison of fitted model result to MRI images at the three time points from Figure 3 following initialization of DI injection (Phase 3). Column A presents corresponding salt concentration profiles, Column B presents the two-site model best fit, and column C presents the one-site model best fit.
Text for graphical abstract. In situ imaging and mathematical modeling capture the effects of salinity changes on magnetite (Fe₃O₄) nanoparticles deposition and transport in porous media.