Evaluating Colloid Release from Natural and Model Porous Media

2010 Annual Report

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Statement of Critical Regional or State Water Problem

The behavior of colloid-sized particles is of significant importance in natural and engineered systems. In natural systems, colloids comprised of singular and aggregated mineral, biological and organic components are ubiquitous in surface and subsurface waters. Due to their propensity to sorb otherwise sparingly soluble contaminants or in the case of biocolloids, inherent risk, their presence in water poses a potential health risk (McDowell-Boyer et al. 1986; McCarthy and Zachara 1989; Ryan and Elimelech 1996). Colloidal interactions are also important in water and wastewater treatment, chromatographic separation, oil production, extractive metallurgy, lubrication, coating and cleaning (Osipow 1962; Yao et al. 1971; Hiemenz 1986). Consequently, the physical and chemical processes that govern colloid interactions with surfaces have been extensively studied, and significant progress toward identifying processes responsible for colloid deposition has been made (e.g., Elimelech and O'Melia 1990; Song and Elimelech 1993; Lenhart and Saiers 2002; Lenhart and Saiers 2003; Tufenkji and Elimelech 2005). However, considerable uncertainty remains about the mechanisms that govern colloid interactions under unfavorable conditions, characterized by systems with like-charged surfaces, particularly with regard to mechanisms responsible for reversible deposition and colloid release in porous media (Kretzschmar et al. 1999). Knowledge of the fundamental processes that control the deposition, release and subsequent transport of colloidal particles and associated contaminants is crucial to maintaining the quality of ground water that the nearly five million residents of the Ohio (OhioEPA 2000) rely on for their daily needs.

Research Objective

The objective of this research is to evaluate the extent and kinetics of colloid release in water-saturated porous media under conditions selected to promote unfavorable DLVO interactions. The work will couple laboratory-scale experimental work with mathematical models to test existing theory and approaches to model colloid transport. Results of this research will be used to (1) evaluate the importance of the secondary minimum in reversible colloid deposition in systems with like-charged surfaces, (2) test the influence of system conditions (e.g., porous media, porewater velocity, porewater composition and colloid size) on reversible deposition, and (3) test the rigor of existing approaches that account for non-DLVO deposition (e.g., Tufenkji and Elimelech 2004) and examine their application to describe colloid release. Such information is needed to accurately predict colloid mobility and appropriately evaluate filtration technologies for their removal from source waters. Two overarching questions drive this research. They are:

- To what extent does reversible deposition depend upon the presence of the secondary minimum?

- How do system conditions (e.g., grain size, solute composition) influence reversible deposition?

Methods and Procedures

The deposition and mobilization of colloids will be evaluated in a series of bench-scale column experiments. Each experiment will consist of two stages, a deposition stage and a mobilization stage. During the deposition stage, a solution comprised of the colloids, suspended in a solution containing simple electrolytes (e.g., 0.01 M NaCl at pH 8), will be introduced into the column as a pulse. The concentration of the electrolyte and the valence of the cation in the influent suspension will be varied between experiments and a suite of experimental conditions will be tested in order to prepare columns that have different retained colloid profiles. Colloids deposited in the column during the first stage will be mobilized through a single, or through successive step-changes in the porewater electrolyte in the second stage. At the conclusion of each experiment, and for some experiments at the conclusion of the deposition stage the porous media will be extruded from the column and the profile of retained colloids will be measured.

Preparation and Characterization of Experimental Materials. Soda-glass beads and/or quartz sand will be used as the porous medium in all experiments. At least two fractions will be isolated for use with nylon sieves. As received, the media may be coated with metal oxides (Fe, Al and Ti) and trace quantities of organics. These impurities will be removed because they may influence surface charge characteristics and thus may promote colloid deposition (Litton and Olson 1993). Upon cleaning, the size and surface charge of the media will be evaluated via scanning electron microscopy and electrophoretic mobility measurements of native colloids (or streaming potential), respectively.

Surfactant-free fluorescent spherical latex particles will be used in all experiments as the colloidal phase. Carboxyl-modified surfaces are commonly used and the sizes chosen will depend upon whether deposition within the primary or secondary minima is to be accentuated. For example, Tufenkji and Elimelech (2005) evaluated the transport of 63, 320 and 3000 nm latex particles through 328 μm soda glass beads as a function of pH and ionic strength. Their results suggest that deposition within the primary minimum is highly unlikely for the 3000 nm particles, but possible for the same particles within secondary minimum. For the 63 nm particles, however, it is expected that conditions favor deposition within the primary minimum. Based on this interpretation, I suspect that compared to the 63 nm particles that the 3000 nm particles would be more amenable to release.

The manufacturer-reported diameter will be confirmed by dynamic light scattering. Latex colloid suspensions will be prepared by adding aliquots of a concentrated stock to the electrolyte solution to achieve the target colloid concentration. The average zeta-potential of the colloids in the different electrolyte solutions will also be determined on the basis of measured electrophoretic mobilities and the tables of Ottewill and Shaw (1972) or the Smoluchowski equation (Hunter 1981).

Column Design. Experiments on the transport of the latex microspheres follow the methods outlined by Lenhart and Saiers (2003). Glass chromatography columns with an internal diameter of 4.8 cm or 2.4 cm and PTFE end fittings will be used to contain the porous media. Depending

upon the desired flowrate a digital peristaltic pump or liquid chromatography pump will be used to control the flow of colloid and electrolyte solutions. The pump will be positioned at the base of the vertically oriented columns and the flow will be directed downward. Each experiment will use a fresh column prepared by wet-packing methods (Lenhart and Saiers 2003). The column will be packed to a predetermined height, and vibration will be used during packing to minimize air entrapment and the formation of layers. The porosity and pore-volume of each packed column will be measured using standard methods.

Column Experiment Methodology - Stage 1: Colloid Deposition. Each packed column will be pre-equilibrated with the electrolyte solution by pumping approximately 10 – 20 pore volumes of colloid-free electrolyte solution through the column prior to commencing the experiment. Colloid concentrations will be monitored in the column effluent during this period to verify that native colloid mobilization is negligible. The equilibration period will cease when the effluent pH matches that of the influent solution. Following column pre-equilibration, a suspension of latex colloids in electrolyte solution will be pumped into the column for a specific period of time (e.g., 2.5 pore volumes), whereupon the colloid-free electrolyte solution will be redirected into the column. Effluent colloid concentrations will be monitored in effluent samples collected with a fraction collector based upon fluorescence intensity or UV/Vis absorption, depending upon the particle size. Experiments will be conducted for different packing heights, electrolyte concentrations, porewater velocity and colloid concentration.

Column Experiment Methodology - Stage 2: Colloid Mobilization. Colloid mobilization will be induced at the conclusion of the deposition stage, when the effluent colloid concentrations return to baseline levels, by perturbing the composition of the electrolyte solutions to increase repulsive double-layer interactions between the colloid and media surfaces (e.g., by diluting electrolyte concentration). Successive perturbations will be examined, depending upon the initial conditions, as will the magnitude of the change in the electrolyte composition. The concentration of the electrolyte in the effluent will be monitored using a conductivity probe or specific ion electrode.

Measuring Retained-Colloid Profile. At the conclusion of each experiment the columns will be drained, disassembled, and the column packing will be extruded in order to measure the profile of retained colloids. A procedure developed by Bolster et al. (1999) will be followed. Upon extrusion, the porous media will be separated into sections approximately 1-cm in depth. These sections will be transferred into centrifuge tubes and appropriate volumes of 1 mM NaOH will be added. The samples will be equilibrated end-over-end for several hours to effect colloid release and then vigorously shaken using a vortex mixer to disperse the colloids throughout the solution. Aliquots of the supernatant will be removed, filtered (if necessary) and analyzed by fluorescent emission or UV/vis absorption. The solids will then be rinsed several times, oven-dried and weighed.

Interaction potential. The basic framework used in estimating the net or total potential energy between suspended colloidal particles or between colloidal particles and collector surfaces follows DLVO theory by summing van der Waals forces (ϕ_{VDW}) and electrostatic double layer forces (ϕ_{EDL}) (Derjaguin and Landau 1941; Verwey and Overbeek 1948). Hogg et al. (1966) derived expressions for electrostatic double layer interactions (ϕ_{EDL}) between two surfaces separated by a solution containing dissolved ions using a linearized approximation of the Poisson-Boltzmann equation. Although Hogg et al. (1966) stipulate the approximation is appropriate for surface potential less than 60 mV, Russel et al. (1989) state that it remains valid up to electrolyte concentrations of 1 M and surface potentials of 200 mV. Equations are

available for both sphere-plate and sphere-sphere interactions, and the expression for two non-identical spheres is given by (Hogg et al. 1966). Van der Waals forces, resulting from the interaction of dipoles, can be estimated assuming pair-wise additivity of the interatomic potentials (Hamaker 1937). At separation distances between the two surfaces greater than a few nanometers, the original Hamaker approach must be modified to account for a reduction in ϕ_{VDW} due to phase-shift between dipoles. To estimate the retarded ϕ_{VDW} I plan to use the expression of Gregory (1981). This equation was originally intended for separation distances less than $0.2r_C$ (Gregory 1981), but its accuracy can be verified for greater separation distances by comparison to the more rigorous expression for retarded ϕ_{VDW} from Czarnecki (1979). The total interaction energy is determined by summing the expressions for electrostatic and van der Waals interactions.

Model for Colloid Transport in Saturated Porous Media in Steady-State Conditions. The model presented by Lenhart and Saiers (2003) will be used to evaluate colloid transport. This model ties colloid release to a critical solute concentration where the barrier to colloid release vanishes. It couples equations to account for the transport of solute and colloids with a mass balance equation to account for the deposition and subsequent release of colloids. To account for distributed release of colloids as a function of solute concentration the model assumes surface irregularities in terms of potential or shape induce heterogeneities in the interaction energies between deposited colloids and the mineral grains. This heterogeneity is accounted for by dividing the immobile-phase colloid population into a series of compartments, where each compartment releases colloids at a characteristic critical solute concentration. The model can describe (1) the transport and deposition of colloids, (2) the consequent profile of the deposited colloids, (3) solute transport, (4) colloid release coupled to porewater solute concentrations, and (5) colloid release across a range in porewater solute compositions.

Progress Summary
Work over the past year comprised (1) characterizing the materials for use in the experiments and (2) collecting experimental data evaluating the transport of latex microspheres with a nominal diameter of 40 nm.

Principal Findings
Materials for use in the experiment comprise a uniform porous media and colloid suspension. The porous media identified for use in the research is quartz sand purchased from Unimin Corp. versus soda lime glass beads. Quartz sand provides a more chemically stable surface and based upon scanning electron images is nearly spherical. The fraction of the sand between 250 μm and 300 μm was isolated using stainless steel sieves. This sand fraction was cleaned after sieving using the sequential acid and base washing protocol. The colloids identified for use in this research (surfactant-free fluorescent microspheres) will be purchased from Interfacial Dynamics Corporation. These particles are hydrophobic in nature and have a chemically stable carboxylate-modifed surface.

The size and electrophoretic mobility of the quartz sand and latex microspheres were evaluated across a range of system conditions. Two sizes of latex microsphere were purchased and analyses of their size using scanning electron microscopy were similar to those reported by the manufacturer of 36 nm and 490 nm. For the sand, particles of small size suitable for evaluation using dynamic light scattering were collected by subjecting a portion of the sand immersed in

deionized water to ultrasound. The microspheres were dialyzed prior to being evaluated. The electrophoretic mobility for both the sand (Figure 1) and latex microspheres (Figure 2) were negative and decreased in magnitude with increasing ionic strength to become less negative. Increasing pH resulted in more negative mobility values.
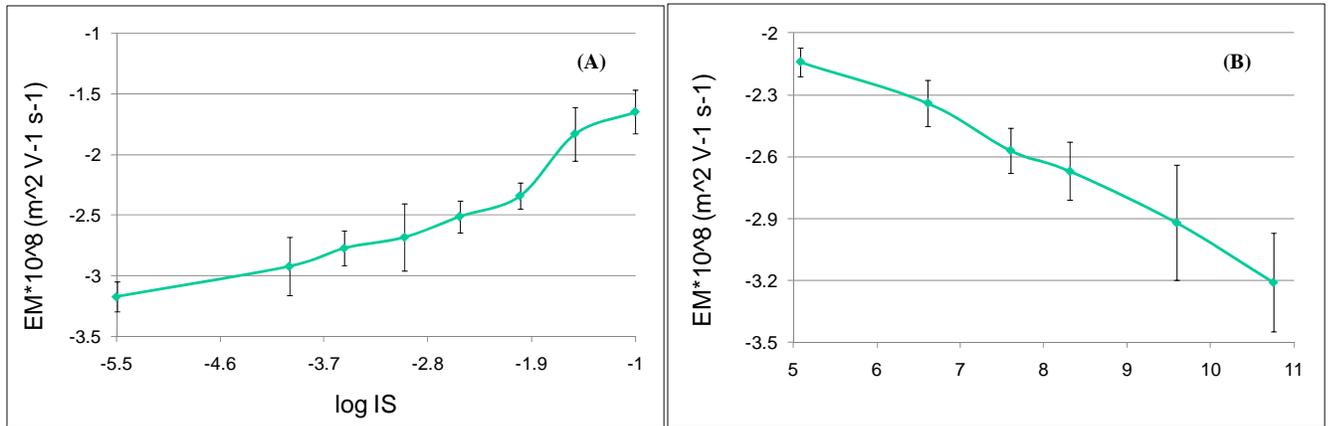

Figure 1 – Electrophoretic mobility of colloid-sized quartz sand particles as (A) a function of ionic strength at pH 7 and (B) a function of pH at an ionic strength of 0.001 M.
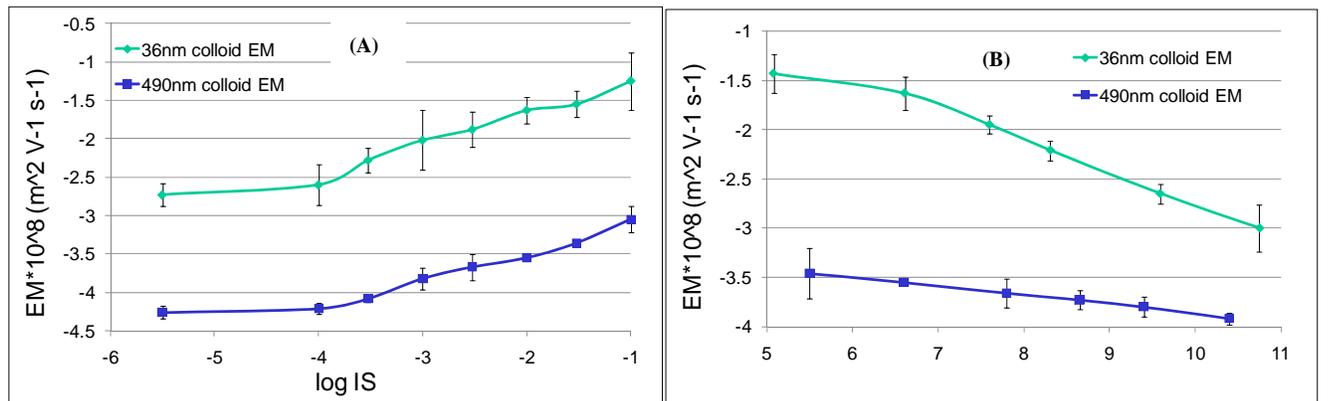

Figure 2 – Electrophoretic mobility of 40 nm latex microspheres as (A) a function of ionic strength at pH 7 and (B) a function of pH at an ionic strength of 0.001 M.

A series of column experiments were conducted with the 36 nm particles as a function of ionic strength. These experiments examined the deposition characteristics and for the conditions with sufficient deposited particles the release was also investigated by systematically altering the solution composition to produce conditions favorable for release by (1) reducing the ionic strength and (2) increasing the pH.

At low ionic strength the transport of the particles nearly matched that of the conservative tracer, bromide (data not shown), indicating little deposition occurred (Figure 3A). With increasing ionic strength, the extent of breakthrough decreased as electrostatically repulsive interactions between the particles and sand were reduced. At an ionic strength of 0.03 M, the breakthrough was further reduced and shifted to longer times, suggestive of behavior similar to solute

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adsorption. At an ionic strength of 0.1 M, breakthrough was significantly suppressed and at 0.3 M no breakthrough was observed (data not shown). Release of the particles was not induced by a reduction in the ionic strength of the solution, which was again consistent with irreversible deposition of the particles in the primary energy well (Figure 3B). An increase in the solution pH from 6.5 to 9.5 did produce a small pulse of released particles (Figure 3B). This suggests that there was a small amount of attractive interactions at the quartz surface consistent with the presence of metal oxides.
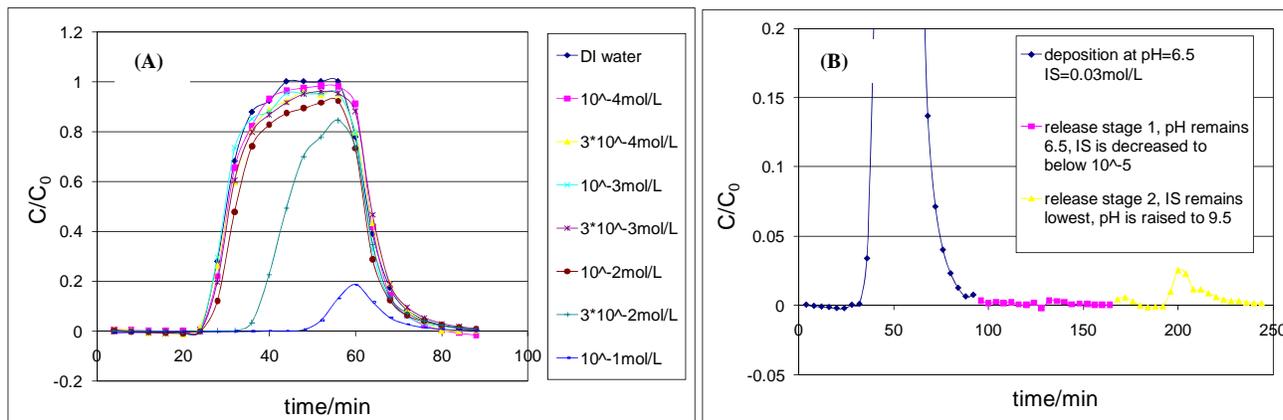

Figure 3 – (A) Transport of the 36 nm particles through water-saturated quartz sand as a function of ionic strength at pH 6.5. (B) Release of particles retained at the conclusion of the deposition of the particles at an ionic strength of 0.03 M resulting from a decrease in the ionic strength of the solution followed by an increase in the pH.

Future work consists of evaluating transport of the 490 nm particles as well as the development of a model to describe the release data.

Publications
Ye, Q., Lenhart, J.J., 2010, "Quantifying the Role of the Secondary Energy Minimum on Colloid Transport and Release in Porous Medium", Presented at the *239th ACS National Meeting*, San Francisco, CA.

Students Supported
Qing Ye (M.S. student in the Department of Civil and Environmental Engineering and Geodetic Science)

Awards or Achievements
None at this time.

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