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Final Report

Project Title: Surface Chemistry Investigation of Colloid Transport in Packed Beds

Principal Investigator: Terese M. Olson, Associate Professor

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Address/Institution: Department of Civil & Environmental Engineering, University of California, Irvine, California 92697-2175

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Project Scope and Objectives

The importance of colloids as co-transport agents for pollutants in subsurface systems hinges on the extent to which electrostatic or other sources of repulsive colloid-collector interactions inhibit their filtration. When electrostatic interactions are favorable, for example when the colloid and groundwater media have opposite charge, colloids may be expected to travel only a few centimeters in saturated porous media. Repulsive electrostatic interactions between colloids and aquifer media with the same charge sign are postulated to significantly mobilize particles [1,2]. As it happens, however, theories describing particle filtration from first principles, i.e., DLVO (Derjagin and Landau, Verwey and Overbeek) theory, dramatically underestimate filtration rates when colloid-collector interactions are electrostatically repulsive [3,4].

One of the primary objectives of the project was to experimentally investigate potential reasons for the historical lack of agreement between particle filtration models based on DLVO theory and observed particle deposition rates. An important hypothesis of the study was to test the validity of the assumption of surface homogeneity, as required by these models. The approach was to focus on collector surfaces that were commonly used as model systems, e.g., glass beads and quartz sand. Laboratory-scale column filtration experiments were conducted with colloidal polystyrene latex spheres. Collector surface preparation and cleaning approaches were examined, as well as the effects of solution chemistry. The results of these investigations are described under "Task 1" below.

Non-electrostatic repulsive forces are well known to stabilize particle suspensions in many industrial and commercial applications, particularly those that arise from polymer coatings [5]. The role of natural polymers in stabilizing colloids with respect to filtration in groundwater systems, however, is not well understood.

The second major objective of the project was to investigate the influence of humic matter and other selected polyelectrolyte coatings on deposition rates in porous media, using colloids of environmental interest - iron oxide particles. Specifically we sought to determine the nature of the repulsive interaction forces that stabilize humic-coated particles and thereby identify the most important general features of humic molecules and solution chemistry variables that influence particle transport. This phase of the project was also designed to complement other DOE field projects, specifically the Georgetown, S.C. colloid transport studies conducted by John McCarthy's group at ORNL. For example, many of the same materials used in the ORNL field study, including natural organic matter isolates and iron oxide particles, were used in our project. These efforts and accomplishments are described under "Task 2" below.

Results and Accomplishments

Task 1. Experimentally determine the importance of collector surface heterogeneity in controlling particle deposition rates.

Several model systems, including spherical glass beads and ultrapure quartz sand, were utilized as filter media to assess whether filtration rates in the presence of electrostatically repulsive interactions were also a function of non-electrostatic factors. Particular attention was given to the importance of collector cleaning and preparation methods. Particle filtration rates were extremely sensitive to bed media preparation methods, despite the similar electrophoretic mobilities of the bed media. The results of these filtration experiments, which are described in Papers #7 and #8 of the *Project Bibliography*, illustrate the importance of non-electrostatic factors. It was postulated that microscale surface heterogeneity is an important overlooked variable that affects filtration rates when overall particle-surface interactions are apparently unfavorable.

Additional experimental evidence that collector surface heterogeneities serve as favorable deposition sites for particles was obtained by masking favorable sites with surfactants. With the addition of anionic surfactants, colloid filtration rates were much more sensitive to solution ionic strength, as DLVO theory suggests they should be (see Paper #4). Particle deposition rates in the presence of surfactants were also found to be particle-size dependent (see Paper #1), unlike previous studies in the absence of surfactants in which filtration was insensitive to particle size [6]. Gary Litton's presentation of these findings at a National ACS Meeting in San Diego was awarded an ACS Certificate of Merit.

Other investigators have since shown using theoretical approaches that collector surface heterogeneity could explain the differences between observed colloid filtration rates and the predictions based on DLVO theory [7]. The data from our experimental studies (Paper #7) was in fact modeled in this theoretical study and used as further evidence that the heterogeneity explanation is likely to be the correct one.

In addition to exploring reasons for the well-known underestimation of particle attachment rates by DLVO theory, we have also determined that there are conditions in which these models *overestimate* colloid deposition rates. Anomalous repulsive interaction forces are evident, for example, between latex colloids and quartz filter media if one of the interacting surfaces is uncharged. These results were summarized in paper #5. In natural systems, the conclusions of this study may be of particular importance in explaining the transport behavior of some bacteria, since the van der Waals attractive forces between bacteria and aquifer solids are likely to be similar to those between polystyrene latex and quartz.

Task 2. Mechanistically examine the role of natural organic matter coatings in stabilizing colloidal particles with respect to filtration.

Pure Fe(III) oxide particles typically have isoelectric points (pH_{IEP}) in the range of 8 to 9. The pH_{IEP} of quartzite sands is less than 3. Thus at neutral pH, pure iron oxide colloids would interact favorably with quartzite aquifer media. Iron oxide particles, however, are good adsorbents of negatively charged natural organic matter (NOM). Once adsorbed, the overall charge of the polyelectrolyte-coated particles is commonly negative. Stabilization of NOM-coated particles, with respect to both coagulation [8-10] and filtration [11-14], was well documented in the literature. The mechanism, however, was not well understood. Polyelectrolytes, such as natural humic matter, can stabilize suspensions by electrostatic and non-electrostatic repulsion [15]. Our experiments sought to determine the mechanism(s) by which this stabilization occurred.

Filtration experiments were conducted with synthetic hematite particles coated with several sources of humic and fulvic acids and fractions of these materials. The suite of organic coatings included a fulvic acid sample isolated from a Georgetown, S.C. surface water and reference samples from the International Humic Substance Society. The Georgetown NOM isolate had been used in field injection experiments by John McCarthy's ORNL group. All of the humic matter samples were extensively characterized by our group and elsewhere. For a given solution chemistry, attachment efficiencies of the coated hematite particles were observed to vary significantly between the different NOM isolates. Smallest attachment efficiencies were consistently associated with the largest molecular size humic material. In the presence of high salt, i.e., negligible electrostatic repulsion, attachment efficiencies of humic acid coated hematite were still much less than unity - suggesting that non-electrostatic forces also stabilize humic acid coated particles. The results of these experiments are summarized in Paper #6 in the *Project Bibliography.*

The initial experiments were conducted in the presence of varying amounts of NaCl as the background electrolyte. Other divalent cations in groundwater, however, could potentially play a more complex role. Divalent cations such as Ca^{2+} are known to specifically bind with electron donor groups in humic acid. These reactions would cause charge neutralization and possibly cation bridging of several humic molecules. Column transport experiments with humic-coated hematite particles in the presence of Ca^{2+} suggested that charge screening and specific binding are both likely to play an important role in controlling particle deposition rates. It was also noted that calcium tends to reduce the deposition rate differences for particles with different types of humic coatings. Included our comparison were coatings consisting of peat soil humic acid, peat soil fulvic acid, and the fulvic acid fraction of the Georgetown injection water NOM. Our results (see Paper #2), together with the ambient groundwater composition of the ORNL Georgetown field site, implicated Ca^{2+} as an important cation in controlling particle transport in field injection experiments.

Mechanistic interpretations of the filtration experiments with humic-coated hematite are hindered by the fact that the parent particle charge and the solution conditions can not be varied independently. In order to vary the surface charge of a metal oxide from positive to negative, it is necessary to change the pH. The extent of protonation of the adsorbed humic matter, and thus its conformation, are unavoidably varied by this pH change. In addition, the surface charge of the quartz media is also a function of pH. To separate these effects, we compared the attachment efficiencies of two humic matter-coated polystyrene latex particles with different surface charge groups - positively-charged amidine groups and negatively-charged sulfate groups, at the same pH. Our results, as summarized in Paper #3, suggest that changes in adsorbed humic matter conformations, which are solely due to differences in the parent particle surface charge, lead to significantly different attachment efficiencies even though the zeta potentials of the coated particles are similar. The greater stability of humic matter-coated sulfate latex was attributed to the more extended conformations of negatively charged humic matter on a negatively charged surface. Under these conditions, repulsive steric and electrostatic interaction forces can more effectively override short range van der Waals attractive forces.

Student Training

The research of two doctoral students was funded under this project. Gary Litton completed his Ph.D. in 1993 and is a Professor at the University of the Pacific in Stockton, CA. Aria Amirbahman completed his Ph.D. in 1994 and accepted a postdoctoral fellowship at EAWAG-ETH (Dubendorf, Switzerland). Their doctoral dissertations are listed in the *Project Bibliography.*

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2. Amirbahman, A.; Olson, T.M. (1995) "Deposition Kinetics of Humic Matter-Coated Hematite in Porous Media in the Presence of Ca^{2+}", *Colloids and Surfaces, A,* 99:1-10.
3. Amirbahman, A.; Olson, T.M. (1995) "The Role of Surface Conformations in the Deposition Kinetics of Humic Matter-Coated Colloids in Porous Media", *Colloids and Surfaces, A*, 95:249-259.
4. Litton, G.M.; Olson, T.M. (1994) "Colloid Deposition Kinetics with Surface Active Agents: Evidence for Discrete Surface Charge Effects", *J. Colloid Interface Sci.,* 165:522-525.
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Conference Papers

Olson, T.M; Chao, J.T., "Deposition of Hematite in Porous Media with Model Polyelectrolyte Coatings", 69th Colloid and Surface Science Symposium, ACS, Salt Lake City, Utah, June, 1995.

Amirbahman, A.; Olson, T.M. "Transport of Humic Matter-Coated Hematite in Packed Beds of Quartz: Role of Calcium", ACS National Meeting, San Diego, Calif., March 1994.

Litton, G.M.; Olson, T.M. "Indirect Evidence for Discrete Surface Charge Effects on Colloid Deposition Kinetics with Sodium Dodecyl Sulfate", ACS National Meeting, San Diego, Calif., March 1994.

Amirbahman, A.; Olson, T.M. "Transport of Humic-Coated Particles in Packed Beds: Effect of Molecular Size", EOS, 73:166, AGU Meeting, December, 1992.

Litton, G.M.; Olson, T.M. "Colloid Transport in Porous Media and Approaches to Examine the Importance of Surface Heterogeneity", EOS, 73:166, AGU Meeting, December, 1992.

Walker, H.W.; Grant, S.B. "Investigation of the Effects of Model Polyelectrolyte Coatings on Colloid Transport in Porous Media", EOS, 73:166, AGU Meeting, December, 1992.

Amirbahman, A.; Olson, T.M. "Deposition Kinetics of Humic-coated Hematite in Packed Beds", 66th Colloid and Surface Science Symposium, ACS, Morgantown, W. Virginia, June, 1992.

Olson, T.M.; Litton, G.M.; Amirbahman, A. "Colloid Transport in Porous Media with Repulsive Energy Barriers", Conference on Interfacial Phenomena in the Environment, Davos, Switzerland, October, 1991.

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Litton, G.M. "Colloid Transport in Packed-Bed Columns with Repulsive Energy Barriers", ASCE Environmental Engineering Division, Univ. of Nevada, Reno, 1990.

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Litton, G.M. (1993) *Colloid Transport in Packed Beds with Repulsive Interaction Energy Barriers,* Ph.D. Dissertation, University of California, Irvine.

Amirbahman, A. (1994) *Transport of Humic Matter-Coated Colloids in Packed Beds*, Ph.D. Dissertation, University of California, Irvine.

ATTACHMENTS

(*Peer-reviewed Publications*)

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