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Project Title: Investigation of the Effects of Polyelectrolyte Coatings on Colloid Transport in Porous Media

Principal Investigator: Terese M. Olson, Assistant Professor

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Address/Institution: Department of Civil Engineering, 101 ICEF
University of California
Irvine, California 92717

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Progress Summary

Scope and Objectives

The primary goal of this research is to determine the nature of the repulsive interaction forces that exist between humic-coated colloids and negatively charged porous media surfaces. Repulsive interaction forces between polymer-coated surfaces are known to arise due to electrostatic and steric repulsion. Through colloid filtration experiments, we seek to determine the relative importance of these two force components, where the primary "polymer" of interest is natural organic matter and the colloid is an iron oxide (hematite). Steric repulsive energies must be further resolved in terms of an enthalpic and an entropic component, in order to obtain a complete mechanistic understanding of the variables that control colloid attachment rates. Repulsion due to enthalpic mixing energies of polyelectrolyte layers of an approaching colloid and collector surface, for example, is likely to be a function of the acidity and polarity of the polyelectrolyte. Entropic repulsion, on the other hand, arises upon the loss of configurational entropy as polyelectrolyte layers interpenetrate or become compressed. Molecular size, rigidity, and surface conformation, therefore, are variables which are likely to most influence the magnitude of this component.

If steric repulsion is an important stabilizing factor in the presence of NOM coatings, other relevant variables that lead to increases in the adsorbed layer thickness, must be considered. Divalent cations, for example, are known to increase the adsorbed NOM layer thickness by cation bridging mechanisms. Based on coagulation studies, they have also been shown to enhance the stability of humic-coated colloids (Tipping and Higgins, 1982). Their effect on colloid filtration rates, however, has not been studied and is being considered as a joint ORNL/UCI effort.

Changes to the scope of the original workplan are proposed to more closely focus the emphasis of the project on natural organic matter systems. Specifically, it is proposed that some of the model polyelectrolyte coatings be replaced by additional studies with NOM-coatings, and that the remaining model polyelectrolytes be limited to a set of copolymers that potentially represent closer analogs to humic materials. These experiments are described below. Some of the original objectives have also been refined and they are enumerated here with brief progress summaries for each.

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Task 1. Determine whether steric repulsion, relative to electrostatic forces, is important in controlling the transport of NOM-coated iron oxide colloids in silica bed media.

Progress. Filtration experiments comparing several humic substances as coatings, including a fulvic fraction isolate from ORNL's Georgetown injection water, have already indicated that steric repulsion is important in enhancing the mobility of colloids in quartz bed columns, particularly at higher ionic strengths, for unfavorable NOM adsorption conditions, and for larger molecular size NOM fractions. These results appear in a publication (Amirbahman and Olson) that has been submitted to *Environmental Science and Technology* (see attachments).

A few additional experiments are still underway to compare the filtration efficiencies of the humic-coated hematite colloids with those of hematite colloids that have been stabilized with a specifically adsorbed anion, phosphate. We expect that these comparisons will help to exactly differentiate between solution conditions under which electrostatic and steric repulsion dominate. The results and analysis of these comparisons are the subject of a separate publication, now in preparation.

Task 2. Determine the nature of the steric repulsive force, i.e., evaluate whether enthalpic and/or entropic energies are important components of the steric repulsive force.

Progress. Our filtration experiments suggest that molecular size, as demonstrated with different size fractions of NOM, and possibly conformation are important factors that control their transport in porous media, and hence for large molecular humic acid coatings, entropic repulsion appears to significantly enhance colloid transport. Preliminary findings also suggest that smaller molecular size fractions can effectively enhance colloid transport in rough proportion to the acidity and/or polarity of the NOM, and thus enthalpic repulsive forces are potentially important. These results are presented with the results from Task 1 in a submitted journal paper.

Additional experiments, to be conducted jointly with ORNL, are still planned to further define the role of NOM acidity in controlling colloid attachment, where both UCI and ORNL will utilize the same NOM isolates of different acidities. McCarthy's group at ORNL, however, will focus on changes in NOM adsorption mechanisms.

Task 3. To ascertain whether cation bridging mechanisms can significantly enhance colloid transport in the presence of NOM.

Progress. Experiments are currently being coordinated with McCarthy's ORNL group, in which the effects of Ca^{2+} will be studied from the perspective of its effect on adsorption mechanisms at ORNL, and from the vantage point of effects on colloid attachment efficiencies at UCI.

Task 4. To investigate and compare the role of cation hydration on the attachment efficiency of NOM-coated and uncoated hematite colloids.

Progress. An additional set of experiments to determine the importance of cation hydration size on colloid attachment efficiencies is proposed to answer mechanistic questions raised in recent filtration studies with humic-coated hematite. These experiments are described in the "Approach" section and will be completed during the second year of the contract. The relevance of this study is discussed under the section "Relevance to DOE Objectives".

Task 5. Evaluate the degree to which selected model polyelectrolytes represent potential analogs for humic coatings in affecting colloid transport. The objective will be to determine whether copolymer coatings yield the same primary features of colloid attachment when specific properties, such as molecular size, acidity, or polarity, are closely controlled.

Progress. These experiments, described below, will be undertaken after completing Tasks 1, 2, and 3.

Approach

Tasks 1 and 2. The approaches taken to address the completed aspects of these objectives have been outlined in an attached paper. The uncompleted portion of Task 2 is to be conducted jointly with the ORNL group and will involve comparing the filtration efficiencies of hematite particles that have been coated with NOM fractions supplied by McCarthy. These NOM isolates of the Georgetown sample will be fractions separated on the basis of their acidity, according to the ion retention chromatography method of E.M. Perdue (Georgia Inst. of Technology). We will utilize the spectroscopic results of the NOM adsorption studies which are being carried out at ORNL, to interpret our filtration results. Based on our previous preliminary findings, we expect that particles with the different adsorbed NOM fractions will be electrokinetically similar, but that the most acidic coatings will yield colloids with the lowest attachment efficiencies.

Task 3. The effects of Ca^{2+} on the adsorption mechanisms of NOM and the transport of humic-coated hematite in porous media will be examined jointly by UCI and ORNL. In our laboratory, filtration experiments with NOM-coated hematite will be conducted for varying $[\text{Ca}^{2+}]/[\text{NOM}]$ ratios, and colloid attachment rates will be determined. The NOM source will be from ORNL's Georgetown injection water, and the samples will be provided by ORNL to allow direct comparison with their adsorption results. The spectroscopic studies of adsorption mechanisms (at ORNL) as a function of the Ca^{2+} content, are expected to provide important background information that can be used in interpreting our colloid filtration results. Adsorbed layer thickness measurements (PCS) will also be used for the same purpose.

Task 4. Filtration experiments completed under Task 1 suggest that attachment efficiencies of humic acid-coated colloids have varying sensitivities to solution ionic strength, depending on the pH of the solution. At higher pH, colloid attachment efficiencies are less sensitive to ionic strength. Under these conditions, the sorbed NOM also has a greater density of charged groups. Greater repulsive hydration forces, due to the association of solvated counter cations with these charge groups, may explain the weaker ionic strength dependence. Short range repulsive hydration forces due to solvated cations have been observed between mica surfaces (Pashley and Quirk, 1984), and the solvation radius of counter cations has been shown to correlate negatively with the coagulation rates of humic acids from solution (Ong and Bisque, 1968).

In these experiments, we will examine lyotropic series of monovalent and divalent counter ions, where the size of the solvated ions vary as $K^+ < Na^+ < Li^+$ and $Ca^{2+} < Mg^{2+} \approx Fe^{2+}$. Bridging effects may complicate the role of divalent cations and hydrolysis reactions may affect the role of Fe^{2+} at neutral pH conditions. If colloid deposition rates are sensitive to the type of cation (keeping the valence constant), particularly for monovalent cations, the importance of solvation effects would be demonstrated. In the event that there is little dependence of colloid attachment efficiencies on the type of cation, we can conclude that the role of the counter ion is simply charge neutralization.

Task 5. Experiments outlined in the original proposal with model polyelectrolytes will be refocused to consider only polymer coatings which may mimic the behavior of humic material. Model copolymer systems will be used to determine the importance of the degree of hydrophobicity vs hydrophilicity on the transport of coated colloids. The copolymers will consist of two covalently linked polymer types, such as poly(propylene oxide) (PPO), and poly(acrylic acid) (PAA), in varying ratios such that the size and hydrophobicity can be manipulated. The PPO sections of the copolymer example mentioned here, would anchor the polymer to the surface while the more hydrophilic PAA sections would extend into solution. By varying the PAA/PPO ratio, the degree of hydrophobicity can be closely controlled. Similar approaches have been applied in studies of colloid stability (Einarson and Berg, 1993), but they have not yet been applied to colloid filtration. Particles coated with these polymers will be used in column studies to evaluate the sensitivity of attachment rates to changes in the copolymer structure.

One of the greatest difficulties in developing a mechanistic understanding of the role of NOM coatings in colloid stability and transport is the lack of proven model systems that simulate their behavior. We hope not only to address the need to develop and evaluate candidate model polymers, but to also take advantage of their well-defined properties to elucidate the factors controlling colloid attachment. By conducting the above model system studies, a wide range of potential electrostatic and steric repulsion conditions can be considered, and hence the limits of polymer-induced stability will be established. The design of field demonstration projects involving polyelectrolyte (such as surfactants or humic material) or colloid injection into natural aquifers could also be improved on the basis of our findings, particularly in the area of material selection.

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Results and Accomplishments

Major portions of Tasks 1 and 2 were completed and the results are presented in the attached manuscript (Amirbahman and Olson). In this work, we have concluded that many humic coating properties (molecular size, acidity, polarity, and possibly surface conformation) have an important effect on colloid attachment rates, ***but very little effect on the electrophoretic mobility of the colloid.*** Steric repulsive forces have been proposed to account for these observations. In addition, some humic coatings are more effective in enhancing colloid transport in quartz bed media, than in enhancing colloid stability. We have explained this result in terms of the smaller van der Waals attractive forces that exist between hematite and quartz than between hematite and hematite. This may also be the reason why steric repulsive forces have been ruled out by other investigators studying hematite stability.

Important differences in the colloid attachment rates were also observed as a function of the surface charge conditions of the parent colloid. At $\text{pH} < \text{pH}_{\text{pzc}}$ of hematite, the favorable adsorption of humic material to the positively charged surface renders the surface negative. At $\text{pH} > \text{pH}_{\text{pzc}}$, much less adsorption of NOM occurs on the negative hematite colloid, however, attachment efficiencies for these colloids were significantly lower than those obtained at $\text{pH} < \text{pH}_{\text{pzc}}$. These filtration results are illustrated in Figure 1 for the case of humic acid coated-hematite, in which the experimental attachment efficiencies are plotted at similar electrokinetic conditions (i.e., as a function of the product of the quartz and colloid electrophoretic mobilities). To contrast these filtration results with particles that are stabilized unequivocally by electrostatic forces, additional experiments with hematite colloids that have been stabilized with specifically adsorbed phosphate anions will be conducted. We hypothesize that the pH effects observed with NOM-coated hematite will not be observed for the phosphate-stabilized hematite.

Future Work

By the end of the first project year, we expect to complete Tasks 1, 2, 3 and portions of Task 4. During the second year Task 4 and major portions of Task 5 will be completed.

Relevance to DOE Objectives and Other DOE Projects

At least two joint studies, as described above, are being coordinated between our laboratory and the ORNL group. In one of these studies, the effects of divalent cations on the adsorption and filtration of NOM-coated particles will be studied. In the second, the importance of NOM acidity is being evaluated. Efforts at UCI will focus on characterizing filtration behavior of humic coated particles, while ORNL's group will spectroscopically characterize the surface sorbed NOM. The same materials will be used by both groups to allow direct comparison of systems and to facilitate joint publication of our results. Future research at ORNL, particularly in the area of adsorption mechanisms, will be invaluable in relating our later conformation studies to humic material coatings. Through our completed transport studies with NOM-coated particles and from our experience in cleaning bed media, we have also been able to provide advice and recommendations related to the selection of materials and regarding potentially

interesting adsorption experiment conditions.

The findings from this study are expected to assist other DOE Colloid Subprogram investigators in their endeavors to interpret field and laboratory-scale colloid transport studies. In particular, field studies at ORNL and by Gschwend et al. at MIT, are the most likely to benefit from the results of our experiments. Since we have used an NOM isolate from DOE's Georgetown, So. Carolina injection water to coat our iron oxides, and have compared their transport results with the filtration rates of particles coated with other humic materials, generalizations based on site-specific field results can now be more readily made. The new proposed studies of the effect of cation type will help to characterize the role of native cations at the Georgetown site in controlling colloid transport. The chemical composition of the groundwater at Georgetown, for example, contains comparable mass concentrations of total Ca and Fe, and hence under reducing conditions, it is possible that Fe^{2+} and/or Ca^{2+} could control colloid transport. In the design of future field experiments at Georgetown, we believe our results will provide useful suggestions for selecting experimental conditions.

When steric repulsion significantly reduces colloid deposition, it is also an important force to consider in detachment models. Gschwend's project to study particle detachment in field systems, therefore, would benefit from our work in defining the conditions in which significant steric repulsion is observed.

Budget

The total requested funds for the second year of the project is \$102,000. The indirect cost rate has increased from 0.475 to 0.495. Budget summaries are included in the attached budget form section. Details regarding the unexpended balance are also provided.

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- Ong, H.L. and Bisque, R.E. (1968) *Soil Sci.*, **106**, 220-224.
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Project Bibliography

Journal Publications in Preparation:

Amirbahman, A.; Olson, T.M. "Deposition Kinetics of Humic Matter Coated Hematite Colloids: pH Effects".

Peer-Reviewed Publications:

Amirbahman, A.; Olson, T.M. (199X) "Transport of Humic Matter-Coated Hematite in Packed Beds", submitted to *Environ. Sci. Technol.*

Litton, G.M.; Olson, T.M. (1993) "Colloid Deposition Rates on Silica Bed Media and Artifacts Related to Collector Surface Preparation Methods", *Environ. Sci. Technol.*, **27**, 185-193.

Olson, T.M.; Litton, G.M. (1992) "Colloid Deposition in Porous Media and an Evaluation of Bed Media Cleaning Techniques", in: *Transport and Remediation of Subsurface Contaminants: Colloidal, Interfacial, and Surfactant Phenomena*, eds., Sabatini, D.A., and Knox, R.C.; ACS Symposium Series, **491**, 14-25.

Conference Papers:

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.

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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.

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