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## **Sorption of Colloids, Organics, and Metals onto Gas-Water Interfaces: Transport Mechanisms and Potential Remediation Technology**

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## Sorption of Colloids, Organics, and Metals onto Gas-Water Interfaces: Transport Mechanisms and Potential Remediation Technology

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### Research Objective

Although contaminant sorption at mineral surfaces has received much recognition as a major mechanism controlling contaminant behavior in subsurface environments, virtually no attention has been given to the possibility of contaminant sorption at gas-water interfaces. Moreover, no effort has yet been advanced to optimize such interactions for the purpose of facilitating in-situ remediation. Gas-water interfaces, unlike water-solid interfaces, are mobile. Therefore, associations of contaminants with gas-water interfaces can be very important not only in subsurface contaminant distributions, but also in contaminant transport, and potentially in remediation. The first objective of this research is to develop a quantitative understanding of interactions between contaminants and gas-water interfaces. The anticipated results will provide insights into the poorly understood phenomenon of contaminant interactions with the gas-water interface, and improve our current conceptual models of contaminant behavior in subsurface environments. The second purpose of this research is to explore the possibility of using surfactant stabilized microbubbles for in-situ remediation. Both pump-and-treat, and air sparging remediation methods are ineffective at displacing contaminants in zones which are "advectively inaccessible". Stable microbubbles can migrate beyond preferential flow pathways and enter lower permeability zones by buoyant rise. The microbubbles can deliver oxygen and nutrients for promoting aerobic degradation of organic contaminants, and also deliver surfactants for emulsifying NAPLs.

### Research Progress and Implications

This report summarizes work after 1.5 year of the 3-year project. In pursuing the first objective, significant results has been obtained. Previous researchers have qualitatively shown enrichment of colloids and colloid-associated heavy metals and organic compounds at the surface of oceans and lakes (which controls mass transfer between ocean and atmosphere), in subsurface vadose zones, and in engineered systems. For surface active molecules, changes in surface tension along with changes in solution concentration determine their surface excesses through the Gibbs equation. However, for suspensions of colloids, surface tension changes are often not measurable. Until initiation of this research project, there were no techniques for quantitatively measuring surface excesses of colloids at gas-water interfaces. In this project a simple bubble column method was developed to quantify surface excesses of colloids and colloids-associated molecules at air-water interfaces. In the bubble column, gas is bubbled through a vertical column containing the dilute aqueous suspension (or solution) of the colloids (or solutes). The rising bubbles sorb and carry the surface-active species upwards, then release them back to the solution at the free surface where the bubbles burst. At steady-state, a concentration profile is established along the column length which reflects the balance between upward transport by partitioning onto rising bubbles and downward transport by eddy dispersion. By directly measuring the column eddy dispersion coefficient for given conditions (column dimensions, air flow rate and bubble size) and measuring the steady-state concentration profile, the (interface-bulk) partition coefficient  $K$ , can be determined. To test the bubble column method, the adsorption isotherm constant of sodium dodecyl benzene sulfate (SDBS) obtained with the bubble column method was compared with the value obtained by conventional surface tension measurements. The  $K$  value of  $64 \pm 4 \mu\text{m}$  for the SDBS obtained with the bubble column method is in good agreement

with the  $K$  ( $64 \pm 12 \mu\text{m}$ ) obtained from surface tension measurements. This agreement validated the bubble column technique as a method for determining partitioning of surface-active components at air-water interfaces. The bubble column method is also sensitive enough to quantify surface exclusion of colloids (negative  $K$  values), another very important capability of this method. The very first measurements of surface partition coefficients of two common types of colloids, clay and humic acid (HA) were conducted with the bubble column technique. The soil humic acid (1S102H, International Humic Substances Society) was used at concentrations of 4, 10, and 20 mg L<sup>-1</sup>, in 5 mM Na<sub>2</sub>SO<sub>4</sub> at pH 6. The reproducible measurements of HA concentration profiles resulted a  $K$  value of 18  $\mu\text{m}$ . A systematic study of different types of clay colloids at different pH and ionic strength conditions is still in progress. The initial results indicate that both kaolinite and montmorillonite can have very high surface partition coefficients under certain chemistry conditions, and that kaolinite generally partitions at the air-water interface much more strongly than montmorillonite. The solution conditions of pH 4.0-6.3, and ionic strength \* 1.0 mM are most favorable for partitioning of these clays at the air-water interface. An article describing this work has just been accepted by the journal Environmental Science and Technology. An anonymous reviewer wrote: "This work makes significant contributions to the field of colloidal science, environmental fate and transport, and environmental remediation engineering. The theory and procedures are immediately accessible, repeatable, and to some extent verifiable."

In pursuing the second objective, we have successfully employed previously developed techniques for generating microbubbles, identified suitable new surfactant combinations, optimizing stability of microbubble suspensions, and testing microbubble transport properties through porous media. Microbubble suspensions were generated by mixing a non-water soluble surfactant (Span 60) with a water soluble surfactant (e.g. SDS and Dowfax 8390) using a spinning disk technique. The disk (rotating at 10,000 rpm) produces strong waves on the surface of the aqueous suspension/solution of a combination of non-soluble and soluble surfactants, entrain air/oxygen into the liquid, and the entrained gas subsequently disperses into microbubbles. A microbubble is composed of a gas phase and a shell consisting of Span 60 particles and dissolved surfactant. The sizes of these microbubbles range from less than 1  $\mu\text{m}$  up to 20  $\mu\text{m}$ . Typical concentrations of these microbubble suspensions range up to 109 microbubbles per mL (determined by Coulter Multisizer). Stabilities of the microbubbles as functions of time and dilution were determined. Non-diluted SDS/Span 60 microbubbles were stable for up to seven weeks. The same results were observed for 1/10 dilution in a solution of 1 mM NaCl + 0.5 mM CaSO<sub>4</sub>. For 1/100 dilution the bubbles were stable up to 19 days. The stability of the microbubbles as a function of hydrostatic pressure was also investigated, revealing that pressures in small excess of atmospheric pressure can readily dissolve microbubbles. This indicates that underground injection of the microbubbles generated using our current approach will not be efficient. We are now testing a method to generate microbubbles under controlled higher pressures in order to increase the dissolved and microbubble-contained oxygen concentrations, and improve the pressure-stability of the microbubbles. The breakthrough curves of microbubble suspensions were measured through columns (25 cm long and 2.5 cm ID) packed with sand (250-425  $\mu\text{m}$ ), at flow rates ranging from 0.06 to 6 m/d. These preliminary tests showed slight microbubble retardation, and about 90% microbubble recovery. If the aforementioned pressure stability problem is resolved, we expect that microbubble injection will be useful in certain remediation efforts where it is desirable to deliver oxygen, nutrients, and surfactants to the subsurface, including advectively less accessible zones.

## Planned Activities

1. Complete studies on clay colloids in ideal "clean" systems.
2. Study air-water interface behavior of clays sorted from vadose zone samples (from DOE contaminated sites such as Hanford).
3. Study partitioning of iron oxyhydroxide colloids in both "clean" and contaminated systems.
4. Study partitioning in more complexed systems containing mixtures of heavy metals, natural organic matter, and organic contaminants.
5. Continue to develop the microbubble remediation technique.