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

Principle Investigators: J. Wan & T. Tokunaga

Postdoctoral Investigators: S. Veerapaneni & F. Gadelle

Research Associates: K. Olson & R. Stover

Earth Science Division, Lawrence Berkeley National Laboratory, Berkeley, California

Project #: 55396

DOE Problems Addressed (Objectives)

This research project is designed to address DOE subsurface contamination problems in two aspects: The first is to improve the basic understanding on mechanisms controlling contaminate spatial distribution, fate, and transport in vadose zones, more specifically, to quantify colloid sorption at air-water interfaces in vadose environments (Figure 1). The second aspect of this project 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". The possibility that microbubble suspension injection into groundwater could provide advantages in remediation of some contaminated aquifers is explored. Potential advantages include enhanced delivery of oxygen, and buoyant rise into advectively less accessible zones (Figure 2).

The Gibbs adsorption equation $\Gamma = -\frac{C}{RT}\frac{d\gamma}{dC}$ (1) is useful for molecular species by Measuring surface tension changes, but not for colloids.

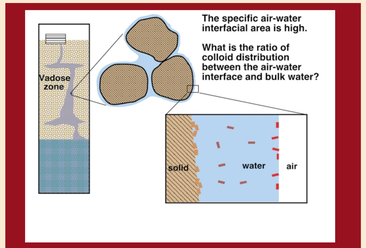

Figure 1. Vadose zone implications of colloid sorption at air-water interfaces. Depending on water film thicknesses and flow, colloid partitioning at air-water interfaces may enhance or retard their transport through the vadose zone.

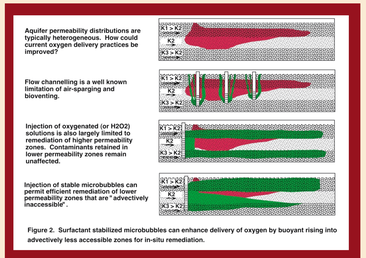

Figure 2. Surfactant stabilized microbubbles can enhance delivery of oxygen by buoyant rising into advectively less accessible zones for in-situ remediation.

Figure 2. Surfactant stabilized microbubbles can enhance delivery of oxygen by buoyant rising into advectively less accessible zones for in-situ remediation.

Part I. Colloid Partitioning at Air-Water Interfaces

Methods Development

A bubble column device (Figure 3) was developed for quantifying colloidal surface excesses. Air is bubbled through the vertical column containing dilute aqueous suspension of the colloids. 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. The steady-state concentration profile reflects the balance between upward transport by partitioning onto rising bubbles and downward transport by eddy dispersion (Eq. 2),

$$af\Gamma = AD\frac{dC}{dz} \quad (2)$$

where a is the average surface area per bubble, f is the bubble generation rate, Γ is the surface excess, A is the column cross-sectional area, D is the column eddy dispersion coefficient, C is the concentration in solution (suspension), and z is the vertical coordinate.

In dilute solutions, partitioning at the water-gas interface is given by $\Gamma = KC$ (3)

For surface-active molecules, K is the linear adsorption isotherm coefficient. In extending this approach to colloid systems, we define K as the colloid partition coefficient. It is expected that in many natural systems the suspended colloid concentration will be sufficiently dilute such that the linear K approximation is sufficient.

The steady-state ratio of the concentration at elevation z versus at the bottom of the column is an exponential profile $\frac{C(z)}{C_b} = \exp\left(\frac{af(K)}{AD}z\right)$ (4)

By predetermining D, a, f, and measuring the steady-state concentration profile C[z], the partition coefficient K can be determined.

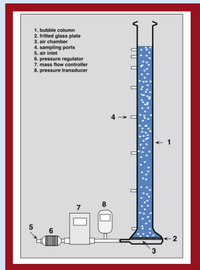

Figure 3a. Bubble column device

Figure 3b. Close-up photograph through the viewing window of the bubble-column, for photographically measuring bubble sizes. The wire inside this section of the column is for scale reference (256 μm diameter).

Verification

The bubble column method was tested by comparing the K value obtained from the bubble column method through Eq. (5), with the K value from surface tension measurements through Eq. (6), for dilute surfactant solutions of sodium dodecyl benzene sulfate (SDBS).

Rearranging Eq. (4) gives $K = \frac{AD}{af}\frac{C(z)}{C_b}$ (5)

Combining Eq. (1) and Eq. (3) gives $K = \frac{-1}{RT}\frac{d\gamma}{dC}$ (6)

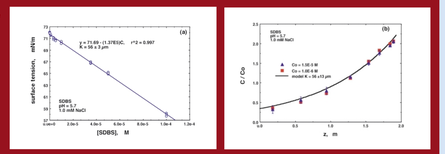

Fig. 4. Testing the bubble column method on SDBS solutions. (a) K = 54±13 μm, from surface tension measurements. (b) K = 54±13 μm, from the bubble column method. This agreement validated the bubble column method.

Examples of Partition Coefficients (K), Which Quantify Colloid Sorption at Air-Water Interfaces

Fig. 5. A) Kaolinite samples taken at steady-state along the verticle-column (pH 5.7). Colloids are highly concentrated at the top, and almost absent at the bottom of the column.

B) Steady-state relative concentration profiles of Na-kaolinite clay particles in the bubble column. Data points are from column experiments conducted at the four indicated pH values. Note that kaolinite partitioning at air-water interfaces varies over a wide range, depending on pH.

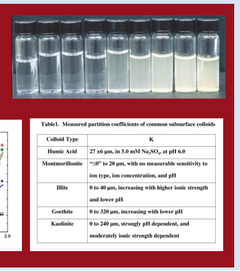

Table1. Measured partition coefficients of common subsurface colloids

Colloid Type	K
Humic Acid	27 ±6 μm, in 5.0 mM Na_2SO_4 at pH 6.0
Montmorillonite	"∞" to 20 μm, with no measurable sensitivity to ion type, ion concentration, and pH
Illite	0 to 40 μm, increasing with higher ionic strength and lower pH
Goethite	0 to 320 μm, increasing with lower pH
Kaolinite	0 to 240 μm, strongly pH dependent, and moderately ionic strength dependent

Conclusions

- We developed a bubble column method for quantifying colloid sorption at gas-liquid interfaces. The method was validated through comparing SDBS K values obtained through conventional surface tension measurements with values obtained with the bubble column.
- The first measured partition coefficients of goethite, kaolinite, montmorillonite, illite, and humic acid at the air-water interfaces are reported.
- This method will permit quantification of surface activities of a wide range of inorganic, organic, and microbial colloids, as well as molecular species complexed onto colloids.

Part II. Generation of Stable Microbubbles and Their Transport Through Porous Media

Microbubble Generation and Characteristics

Microbubbles in the size range of 0.7 to 20 μm are generated by spinning a disk 2-3 cm below the surface of a surfactant solution (Figure 6). The disk, spinning at speeds up to 16,000 rpm, produces strong waves on the surface of the solution, which hit the baffles and entrain air into the liquid. The trapped air subsequently breaks into microscopic bubbles that are stabilized by the surfactants. The microbubble generator is enclosed in a stainless steel chamber to generate microbubbles under pressures up to three atmospheres and allows use of oxygen or other gases. Among several surfactants and their combinations that are tested, the combination of an anionic surfactant (SDS) and a non-ionic surfactant (Span 60) is found to yield the highest concentrations and the most stable microbubbles. The measured concentration and size distribution of microbubbles over time suggests that significant number of bubbles in the size range of 0.7 to 2 μm can last for periods longer than four weeks (Figure 7). Significant loss of microbubbles occurred when they were subjected to pressures greater than that at which they were generated, due to gas solubilization.

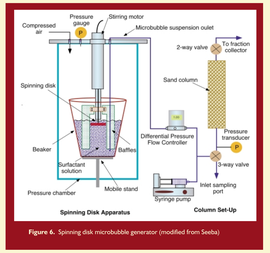

Figure 6. Spinning disk microbubble generator (modified from Seeba)

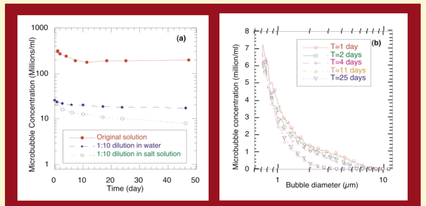

Figure 7. Stability of microbubbles over time: (a) Concentration of microbubbles remaining in solution over time; Salt solution contained 1.0 mM NaCl and 0.5 mM $CaCl_2$. (b) Bubble size distribution of original suspension over time.

Column Experiments on Microbubble Transport Through Porous Media

Transport experiments were conducted in sand columns of three grain sizes: 415-500 μm (coarse), 150-212 μm (medium), and 53-106 μm (fine) under steady flow conditions. One to three pore volumes of microbubble suspensions were injected at atmospheric and elevated pressures of 310 and 340 kPa, followed by a flush with bubble-free solution. A model for microbubble transport in porous media is developed based on one-dimensional convective-dispersive transport equation. Effects of dispersion, sorption, and bubble capture mechanisms have been included in the model based on filtration theory. Transport experiments through coarse and medium sands at atmospheric pressure yielded similar results, exhibiting nearly conservative transport for coarse sand and small loss for medium sand. Typical results of bubble breakthrough curves under atmospheric pressure through a medium sand column are shown in Figure 8. Similar results were observed in five replicate experiments conducted at pressures of 310 to 340 kPa (Figure 9). Higher retention of microbubbles was observed for fine sand columns. Figure 10 shows normalized effluent concentrations and pressure changes for experiments involving injection of 3 pore volumes of microbubble suspensions through medium and fine sand columns. The effluent concentration profiles indicate that retention as well as re-entrainment of bubbles occurs. This is favorable for successful continuous injection of microbubbles without clogging the porous medium. The higher pressures during transport in fine sand is expected because fewer bubbles are needed to block the small pores, compared to the larger pores in medium grain sand.

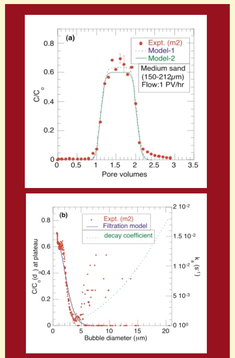

Figure 8: (a) Microbubble breakthrough curve for one pore volume pulse injection at atmospheric pressure into medium sand media (1 PV/hr). ..... Model fit using sorption, dispersion and decay as fitting parameters; ____ Model fit with decay coefficient obtained from filtration (b) Estimation of decay coefficient from filtration theory.

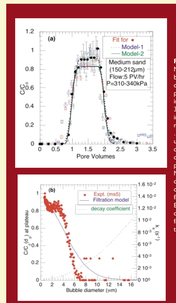

Figure 9: (a) Microbubble breakthrough curve for one pore volume pulse injection at 310-340 kPa pressure into medium sand media (3 PV/hr). ..... Model fit using sorption, dispersion and decay as fitting parameters; ____ Model fit with decay coefficient obtained from filtration (b) Estimation of decay coefficient from filtration theory.

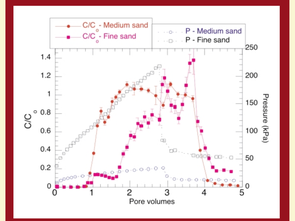

Figure 10: Normalized effluent concentrations through medium and fine sand columns. Three pore volumes of microbubbles have been injected, followed by flushing.

Conclusions

- Generation of stable microbubbles (0.7 to 20 μm) is accomplished using a mixture of sodium dodecyl sulfate and a Span 60, with concentrations up to 3x109 bubbles/mL, specific gas volumes up to 70x109 μm3/mL, and specific surface areas up to 50 cm2/mL. The lifetime of these microbubbles can exceed 4 weeks.
- For one pore volume of injected bubble suspension, effluent recoveries of 100, 80, and 30% were achieved from columns of coarse (415-500 μm), medium (150-212 μm), and fine (53-106 μm) sands, respectively. Effluent recovery increased to 63% following a 3-pore volume injection in the fine sand columns. The experimental results indicated that microbubbles can travel significant distances in subsurface environments.
- Filtration theory was successfully used to model microbubble transport and retention in porous media.

Potential Benefit to EM Science Need

Although the importance of colloid-facilitated contaminant transport has become well recognized, conditions responsible for vadose zone colloid transport have not previously been quantified. Colloids sorbed at air-water interfaces in the vadose zone are potentially highly mobile, yet prior to this EMSP-funded study, no methods for quantifying colloid surface excesses were available. In part one of this study, we developed a bubble column method for measuring partition coefficients of colloids at air-water interfaces. This method permits quantification of surface activities of a wide range of inorganic, organic, and microbial colloids, as well as molecular species complexed onto colloids. Partition coefficients of goethite, kaolinite, montmorillonite, illite, and humic acid at the air-water interfaces were obtained. Our results show that colloid partitioning at air-water interfaces of partially-saturated porous media can be much more significant than previously recognized.

The second part of this project evaluated the possibility of using surfactant-stabilized microbubbles for in-situ remediation. Both pump-and-treat and air sparging methods are ineffective in lower permeability zones that are "advectively inaccessible". Potential advantages of microbubble suspension injection include enhanced delivery of oxygen, and buoyant rise into advectively less accessible regions. We identified some restrictive conditions under which microbubble injection might be effective. Our tests indicate that microbubbles of ≈1 μm size will have favorable mobility in regions with permeabilities higher than 5×10^{-12} m^2. Filtration also imposes severe limits for both much larger and much smaller size microbubbles. Dissolution of microbubbles upon exposure to elevated pressure can be minimized by high pressure microbubble generation

Publications

Wan, J. and T.K. Tokunaga, Film-straining of colloids in unsaturated porous media: conceptual model and experimental testing, Environ. Sci. Technol, 31, 2413-2420, 1997.

Wan, J. and T.K. Tokunaga, Measuring partition coefficients of colloids at air-water interfaces, Environ. Sci. Technol, 32, 3293-3298, 1998.

Veerapaneni, S. , J. Wan, T.K. Tokunaga, Particle motion in film flow, Environ. Sci. & Technol. in press, 2000.

Wan, J., S. Veerapaneni, F. Gadelle, and T.K. Tokunaga, Microbubble generation and transport through saturated porous media, submitted to Water Resources Research, 2000.

Gadelle, F., J. Wan, T.K. Tokunaga, Removal of Uranium (VI) from contaminated Sediments by Surfactants, submitted to J. Enviro. Quality., 2000.

Wan, J., T.K. Tokunaga, Surface excess of clay colloids at gas-water interfaces, submitted to J. Colloid and Interface Science.