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Dear Drs. Massey and Hirsch:

The following is our first year's progress report for DE-FG07-96ER14712, Manipulating Subsurface Colloids to Enhance Cleanup of DOE Waste Sites. If I may provide any further information, please do not hesitate to contact me.

Sincerely,

Philip M. Gschwend

Progress Report (first year): Manipulating Subsurface Colloids to Enhance Cleanup of DOE Waste Sites (DE-FG07-96ER 14712)

October 27, 1997

Introduction

Our research is aimed at (a) developing improved understandings of the processes involved in holding colloids immobile in subsurface media, and (b) exploring the prospects for mobilizing such colloids to enhance cleanups. These colloids are important because they are the chief sorbent media for many contaminants of concern.

The following briefly describes our efforts in the last year. A draft manuscript (currently submitted to Environmental Science and Technology) is also appended.

Mechanisms Controlling Colloid Releases (Swartz)

Using aquifer materials from a Southeastern Coastal Plain site, we have explored the mechanisms which control the releases of attached colloids into the groundwater flow. First, we have completed electron microscopy observations regarding the intimate particle:particle juxtapositions in the solids (Swartz et al. Geochim. Cosmochim. Acta 61, 707, 1997.) Next, by flushing these aquifer sands with various aqueous solutions, we have found that the bulk of the attached colloids appear to be (a) bound to one another via intermediary amorphous iron oxyhydroxides, and (b) attracted to the other colloids by juxtapositions of oppositely charged phases (manuscript submitted to Environ. Sci. Technol. and attached.) We suspect that this combination of inter-colloid interactions may be especially important in geologically “young” deposits where diagenetic processes have not produced highly crystalline solids yet.

As a result of these observations and laboratory manipulations, we believe we understand the steps necessary to initiate colloid mobilization at such a groundwater site. First, one must apply solution constituents which are suited to dissolving a limited portion of the amorphous iron oxyhydroxides. We have accomplished this using 0.5 mM ascorbic acid (i.e., vitamin C.) Next, one must reverse the surface charges of either the negatively charged alumino-silicate clays or the adjacent positively charged iron oxyhydroxides. We have used 0.5 mM phosphate solutions (pH 5.2) to drive the iron oxyhydroxides to a net negative surface charge. By working at only millimolar levels, the resulting total solution ionic strength is still low enough to permit the corresponding expanded “double layers” to push the now like-charge colloids apart. In the laboratory, this results in a sustained presence of about 2 mg colloids per liter of flushing solution for at least many tens of pore volumes.

In our continuing efforts, we have returned to the field site, where the aquifer solids were initially collected, and tested the possibility of using such ascorbic acid-phosphate solutions to mobilize colloids in the ground. Our efforts have proven successful as measured by the presence of turbidity in suitably altered flushing solutions (and the absence of turbidity in control tests.) We are now completing measurements of the ancillary parameters necessary to interpret the field tests.

Studies In Support of the Cleanup of a Chromium-Contaminated Site
(Johnson and Hellerich)

In the last year, we have also pursued studies at a chromium- (and nickel-) contaminated site in Connecticut. First, we have performed coring and well installations. The coring was done to seek a contaminated site suited for an eventual field mobilization test and to begin to define the pre-treatment level of contamination. Our measurements of the aquifer materials shows that the contaminated aquifer still contains about 500 ppm Cr (vs. about 50 ppm background) after (a) continued discharges have been halted, and (b) large volumes of water have been pumped through the site. We have also found that the aquifer materials are contain primarily quartz and mica, with about 2% iron (?oxide) content.

We have utilized these aquifer solids in the laboratory to begin evaluating solutions which can detach colloids and associated chromium. Using about 3 grams of sediment with 20 mL of various dispersant solutions, we mix the suspensions for 1 minute, allow the suspension to settle for 30 minutes, and then sample the supernatant for colloids and metals. Interestingly, solutions of ascorbic acid-plus-phosphate did not cause substantial colloid and chromium releases (as compared to distilled water and inert salt solution controls.) However, a 1 mM borate solution (pH 9.3 vs the site's ambient pH near 6) did cause substantial colloid detachment. Moreover, about one third of the chromium also "detached" and remained bound by the suspended colloids using this borate treatment. We are continuing to study this important result by analyzing the nature of the released solids and exploring the mechanism by which the borate solution enabled release (i.e., was it surface charge reversal?)

Finally, we have been examining the contaminated site's hydrology to locate a suitable locus for an eventual field mobilization test. Using existing wells and those we have added in locations likely to be near the eventual field-mobilization tests, we have particularly examined the influence of a large volume extraction well on the local flows. This well is turned on and off approximately daily in an effort to prevent off-site migration of chromium and related wastes. (We plan to use this well to assure ourselves that any chromium we mobilize upgradient from it will not move offsite.) Our initial findings indicate that we will be able to set up a suitable test area about 30-40 feet upgradient from this well (about 12 to 16 feet 'below the ground surface). Additionally, our slug tests have shown that the hydraulic conductivities in this test area will be about 10^{-4} to 10^{-3} cm/sec, and travel times across a test cell 10 feet long will only be about 3 to 4 hours due to the induced flow field.

Other Project Issues

The project has served as the primary source of support for one post-doctoral associate (Dr. Carol Johnson) and one Masters student (Lucas Hellerich at U. Conn.) Additionally, one Ph.D. graduate student at MIT (Chris Swartz) has derived partial support from this grant. The first year unexpended funds will be $7500 (i.e., about 5.7% of the year's budget). We are pursuing a major ($4000) repair to our ICP, the instrument used for metals' analyses, and we have some outstanding charges (about $3000) derived from our the late-summer field work in South Carolina. Hence, we do not expect that significant funds will remain after the first year's support.