NOTICE

CERTAIN DATA CONTAINED IN THIS DOCUMENT MAY BE DIFFICULT TO READ IN MICROFICHE PRODUCTS.
COLLOIDS IN GROUNDWATER: THEIR MOBILIZATION, SUBSURFACE TRANSPORT, AND SORPTION AFFINITY FOR TOXIC CHEMICALS.

Massachusetts Institute of Technology

FG02-89ER60846

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
TECHNICAL PROGRESS REPORT

Introduction

During the initial project period, we have pursued several activities with the overall goal of characterizing the roles of colloids in groundwater. First, we have collected soil cores from a site where we have previously found large quantities of kaolinite colloids in the groundwater (Ryan and Gschwend, 1990). We have intensely investigated these cores to test our hypothesis that the colloids have been mobilized as a result of iron oxide dissolution. Next, we have constructed a soil core system in our laboratory with which we are attempting to mimic the factors that we think are governing colloid transport in the subsurface. Finally, we have pursued the issue of how well organic chemicals bind to the kinds of colloids that we are seeing at field sites. Together, with our knowledge of colloid mobility, we anticipate that this sorption data will enable us to predict the influence of groundwater colloids on contaminant fates in the subsurface. Our progress in each of these activities is described in more detail below.

Mobilization of Colloids in Response to Iron Oxide Dissolution

The first major objective of our project is to provide a quantitative basis for predicting the abundances of colloids moving in groundwater. From previous studies based chiefly on groundwater samples (Ryan and Gschwend, 1990; Gschwend et al., in press), we have developed the hypothesis that pre-existing soil colloids (e.g., clays) are mobilized as a result of the dissolution of secondary mineral phases that act as cementing agents in the soils or aquifer solids. These secondary phases include iron oxides and calcium carbonates, and we postulate that groundwater flows containing recently introduced reducing agents (e.g., organic compounds) or acid—producing agents (e.g., as derived from the oxidation of organic compounds) titrate these cementitious phases and release colloids bound up by them.

To examine this decementation hypothesis further, we have sought to complement our groundwater observations with data from soil and aquifer solids collected at the same location. Thus, we have returned to the Pine Barrens of New Jersey, and cored at downgradient positions corresponding to
the Swamp and Upland groundwater monitoring wells we have sampled for colloids (Figure 1). These solid samples were obtained by driving a split spoon sampler ahead of the hollow stem auger used to drill the hole. Upon returning to the laboratory, the sediments were examined by a variety of techniques to assess the importance of iron oxides for immobilising kaolinite colloids.

Examination of the aquifer solids using scanning electron microscopy (SEM) and scanning electron microscopy—energy dispersive X-ray analysis (SEM—EDAX) provided strong support for the association of the clay colloids with iron oxides. First, SEM images of the aquifer sands collected from the oxic Uplands core clearly showed regions such as at the contact of larger skeletal grains where fine particles had aggregated (Figure 2). The surfaces of these larger immobile grains were also rough and apparently colloid—coated. Magnification of these positions revealed particles with the appearance of clays (Figure 2). Use of SEM—EDAX confirmed that these aggregates were rich in Fe and Al as we expected for iron oxide—cemented kaolinite colloids. Parallel observations of the aquifer solids from the anoxic Swamp core sharply contrasted the Upland results as the individual grains exhibited quite smooth surfaces and little or no indication of secondary deposits rich in Fe or Al. Thus, the sediment particles reflect the effects of the oxic (Upland) or anoxic (Swamp) groundwater in a manner consistent with our hypothesis.

Mineralogical analysis of these aquifer solids using X—ray diffraction indicated overwhelming levels of quartz in the whole samples. When we used less than 2 µm subsamples, goethite (the iron oxide we expect to act as the secondary cementing phase here) was clearly present in the Upland core, but absent in the sediments recharged by anoxic groundwater from the Swamp.

To confirm and quantify the presence of secondary iron oxides in the Upland core, as well as their absence in the Swamp core, we developed a selective extraction procedure to dissolve only these iron oxide phases and minimally attack structural iron species (e.g., in heavy minerals or as isomorphic substitutions in clays). This method employs a ternary complex, Ti(III)—citrate—ethylene diamine tetraacetic acid, as a reductant and bicarbonate as a pH buffer (Appendix I). The iron oxide dissolution capability of this new method is comparable to the widely—used dithionite—citrate—bicarbonate method of Mehra and Jackson (1980), but it does a much better job of not dissolving
Figure 1: Map showing location of field site and relative positions of monitoring wells (circles) and soil cores (triangles).
Figure 2a: Scanning electron micrographs of aquifer solids from an oxic groundwater zone showing fines aggregated on surface of and at contacts between larger skeletal quartz grains (> 0.1 mm diameter). Right hand micrograph shows collection of fines in blow-up of illuminated area on left.

Figure 2b: Scanning electron micrograph illustrating the uncoated quartz sand surfaces from subsurface regions flushed by anoxic groundwater.
structural iron. Tests of the method using subsamples from our cores emphasise the advantage (Figure 3). In a subsample (3.8.2) containing orange-stained sand from an oxic zone (presumably one with goethite acting as a cementing phase), we see that the solid's total iron is nearly identical to the iron obtained with our new extraction procedure. The small difference is easily understood given the small amount of iron-containing kaolinite and heavy minerals (e.g., pseudo rutile) present in that sample. These results sharply contrast the observations for the anoxic sediment analyses. Here the total iron present greatly exceeds the extractable iron oxide. Since this subsample contained 2.6% heavy minerals, we can entirely explain the difference with structured iron from these primary phases. As a result, we believe we now have a way to analyse for only the Fe-cement in samples containing iron in numerous mineral forms. This quantification of cement—only will be very helpful in characterising the sensitivity of various soils or sediments to changes in groundwater chemistry which may enable colloid mobilisation through iron oxide dissolution. For example, sample 3.8.1 is obviously already "decemented" and colloids should be mobile there, but sample 3.8.2 contains substantial secondary iron oxide cement and would have to be flushed with enough reductant and for long enough to dissolve about 50 μmoles of Fe oxide per gram soil before colloid release would be expected.

Detailed analyses of the cores for Fe, Al, Ti, Mn, and organic C were performed to elucidate how the geochemical cycling of iron could be controlling colloid accumulations in the aquifer solids. The first major result of these analyses in that we realise that the pseudorutile (an iron titanium oxide) currently present probably provides the major source of new iron to act as a cement in this subsurface environment. The presence of the pseudorutile suggests that the heavy mineral, ilmenite (FeTiO₃), was the original supplier of iron to this beach deposit. Assuming ilmenite was the original source of iron, and that the titanium present today may be used to quantify the original abundance of this mineral at any position within the sediments, we can calculate how much iron should occur at these depths were it not carried away by flowing groundwater as Fe(II). Comparison of this "iron source strength" with the iron still measurable at each depth reveals a very interesting difference between the Upland and Swamp cores (Figure 4). For all intervals examined in the Uplands core except the uppermost soil layer, the expected input of iron from ilmenite matches the total iron present. Recall that most of this residual iron is now
Iron in Pine Barrens Swamp Core Samples 3.8.1 and 3.8.2

Figure 3: Iron measured in anoxic (circles) and oxic (triangles) subsamples of aquifer solids from the Pine Barrens. Total iron (filled symbols) greatly exceeds "iron-oxide" iron (open symbols) in the anoxic solids suggesting the limited presence of this cementitious phase in them; most of the total iron seen in the oxic zone solids appears to be in iron oxides.
Figure 4: Comparison of expected iron levels assuming an ilmenite source mineral and present levels of Ti quantify this source strength (right of axis) with the observed iron levels today (left of axis). The Uplands oxic core generally shows a balance of source strength and present-day levels of iron; the Swamp anoxic core suggests most of the iron has been transported away (presumably as Fe$^{+2}$ in the groundwater).
present as iron oxide (deduced with our new selective extraction procedure). In contrast, all depths of
the Swamp core show much less iron than expected from the source heavy minerals. These observations
are consistent with our image that weathering supplies iron throughout the Cohanseay Sand deposit, and
this iron coats the structural grains of quartz as iron oxides whenever the groundwater is oxic. But if
reducing conditions are imposed, the iron oxide is dissolved and carried away, thereby eliminating the
chief factor preventing colloid transport in this type of formation.

To examine these concepts under more controlled conditions, we have also begun to try to
simulate the key processes in our laboratory. We have built a short soil column test apparatus (Figure 5)
in which we have placed a fine quartz sand to mimic the structural conditions of the Cohanseay Sand
formation. Such clean sand does not act as a good filter for kaolinite colloids, as we can readily
demonstrate substantial transport of this clay through our column when applied in a suspension at pH 5
(Figure 6). This laboratory result changes markedly if the column is first washed with an Fe(III)
solution before applying the kaolinite suspension. In this instance we have attempted to simulate the
modification of the quartz surfaces by iron which has been leached from heavy minerals under oxidising
conditions. Now the kaolinite colloids exhibit a much reduced (possibly even negligible) ability to be
transported through the short test column (Figure 7). In our first efforts to simulate the importance of
the iron to controlling the colloid’s transport, we have already seen that the manner in which the iron is
put in place (i.e., time of aging, pH of Fe solution) probably plays an important role in governing its
effectiveness for filtering the colloids. Future efforts need to clarify this and then proceed to demonstrate
how reducing solutions can initiate colloid remobilisation. Subsequently we should be in a position to
calculate the ability of aquifer solids to continue acting as a colloid filter if an anoxic waste plume were
flushing them.

Sorption of Organic Compounds to Inorganic Colloids

Since we have seen substantial quantities of inorganic colloids mobilised in subsurface
environments (e.g., 60 mg kaolinite per liter in New Jersey groundwater, 10–100 mg silicate colloids per
liter in Nevada groundwater), we have also placed a major emphasis on the sorption of hydrophobic
Figure 5: Exploded view of short "soil column" used to test factors controlling colloid transport.
Kaolinite Retention
in Quartz Column

Figure 6: Breakthrough curve for kaolinite colloids applied to clean quartz sand column.