ANIONIC CO-CONTAMINANTS AND THE BIOGEOCHEMICAL EVOLUTION OF AQUIFER HETEROGENEITY

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SUMMARY

Organic acids, chelators, and radionuclide-organic complexes are key contaminants at DOE waste sites. The proposed research addresses a critical need for experimental determinations of the surface and solution interactions of mixtures of these components in naturally heterogeneous aquifer materials. Three related hypotheses are addressed in this project:

Hypothesis 1. Aquifer materials with high chemical heterogeneity exhibit less adsorption competition among solutes because each component adsorbs relatively independently.

Hypothesis 2. An aquifer exhibits the greatest apparent heterogeneity in adsorptivity when it is "pristine". At high concentrations of adsorbates, the magnitude of spatial variability of the effective surface reactivity is diminished.

Hypothesis 3. Certain contaminants cause aquifer adsorptivities to evolve over time, such that the aquifer becomes less heterogeneous. Specifically, dissolution-promoting contaminants preferentially weather the most reactive mineral constituents so that: 1) the total adsorptive capacity declines, and 2) the aquifer evolves toward a more homogeneous state.

The hypotheses are being tested with co-contaminants and subsoils representative of DOE sites. Target solutes are oxalic acid, EDTA, Co(II)EDTA, and natural humic acid. Batch, mini-column, and conventional column methods will be used and results analyzed with numerical models of coupled chemical transport processes. Project findings will be linked to collaborative intermediate- and field-scale studies.

This project is in the first year of a three-year renewal period. The work presented here began in August 1993. The work builds on a previously funded three-year SSP/CCC project ("Adsorption of Chromate/Organic-Acid Waste Mixtures in Aquifer Materials") but represents a distinctly new avenue of research. The new direction was suggested both by the scientific importance of the concepts and by the desire to enhance collaboration and integration with other research initiatives within SSP/CCC.

This report outlines the advances that have been accomplished within this first year. In particular, we have made substantial progress in demonstrating that the heterogeneity aquifer materials indeed evolves over time in the presence of dissolution-promoting co-contaminants.

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I. OVERVIEW

I.A. Original Objectives of Project

The overall goal of the proposed research is to quantify the evolution of mineral-surface reactivity in heterogeneous aquifer materials exposed to mixtures of organic acids, chelating agents, and metal-organic complexes. We will achieve this goal in three stages in which we:

- 1) Develop a more comprehensive understanding of the surface and solution speciation of mixtures of the targeted organic acids and complexes in the presence of representative aquifer adsorbent phases.
- 2) Use this understanding of equilibrium speciation to attack the more critical problem of time-dependent processes: Dissolution/alteration of heterogeneous mineral surfaces and redistribution of elements among solution and surface species.
- 3) Integrate this knowledge into a realistic framework through experiments with an intermediate-scale microaquifer physical model that incorporates well defined heterogeneities.

Our specific objectives are to:

- Document that the dissolution rates of metal oxides in natural and synthetic aquifer materials depend on surface speciation, with an emphasis on competition between dissolution-promoting and non-promoting anions.
- Quantify the importance of solution respeciation and readsorption of Fe(III) to the overall rate of dissolution.
- Test the hypothesis that the surface heterogeneity of natural Fe-oxide minerals diminishes during the course of ligand-promoted weathering.
- Determine whether this diminishing surface heterogeneity increases the intensity of anion competition for surface sites.
- Modify a numerical multicomponent transport to incorporate the time-dependent evolution of the matrix surface.
- Utilize this transport model to interpret and characterize the evolution of transport properties of aquifer materials in experimental flow columns.
- Collaborate with other DOE-sponsored research groups to test the cumulative effects of contaminant-induced weathering by experiments using an intermediate-scale microaquifer containing defined geochemical heterogeneity.
- Document the overall effect of time-dependent evolution of mineral heterogeneity on the transport of Co(II)EDTA in the microaquifer system.

I.B. Current Research Approach

Our primary experimental approach uses laboratory experiments with synthetic aqueous phases and natural subsoil samples. For reference purposes a synthetically prepared Fe-oxide-coated sand is also being examined. Conventional batch and 1D column studies are conducted as well as novel "mini-column" experiments that allow much of the flexibility of batch experiments but which avoid some of the artifacts that plague batch experiments due to the disruption of fines and colloids. Numerical models will be developed and used primarily in a diagnostic mode. That is, modeling will be primarily a tool for interpreting processes observed in relative complex systems subject to open (i.e., flowing) conditions).

II.A Synopsis Of Major Accomplishments In Year 1

- We elucidated the major adsorptive characteristics of two natural subsoil samples and one synthetically oxide-coated sand. These samples are part of the collection of materials being gathered by our collaborators at PNL for use in interdisciplinary studies at a number of SSP/CCC participating laboratories. Our results are available for use by these other research groups.
- We have designed and constructed a novel "mini-column manifold" for studying the surface properties of soils under dynamic flow conditions. The manifold possesses the advantages of both batch and flow-column methodologies. In the present configuration, 22 mini-columns run simultaneously in kinetic studies of the geochemical evolution of sorptive surfaces on the natural and synthetic soils.
- Using conventional batch methods as well as the mini-column manifold, we have demonstrated that the ligands targeted for study by the SSP/CCC induce substantial weathering of subsoil surfaces on time-scales of weeks to months. Our present work with oxalate complements related studies at PNL using EDTA.
- We found that this weathering produces striking changes in the adsorption characteristics of the subsoil samples. Most significantly, the oxalate-induced weathering appears to preferentially attack the strongest binding sites, thereby inducing a time-dependent diminution of surface heterogeneity. This important finding provides preliminary confirmation of one of the major hypotheses of this project.
- Preliminary modeling has reasonably represented the salient features of this geochemical evolution of adsorptive site heterogeneity. By providing a general framework for interpreting the processes, the model results have been useful in suggesting future directions for collaborative work with SSP/CCC researchers at PNL and Oregon State University.
- Conventional flow-columns have been constructed containing each of the natural subsoils and the synthetically coated sand. One column contains layers of all three materials to investigate systems with known heterogeneity at the

REV scale. These columns are being weathered by exposure to dilute oxalate solutions as in the mini-column manifold, but they provide information complementary to that obtained from the manifold. In particular, the column studies explicitly focus on changes in the transport properties of metal-ligand mixtures in a natural porous matrix undergoing geochemical surface evolution. The column experiments are anticipated to be the bridge to collaborative meso-scale transport studies with PNL.

II. PROJECT ACCOMPLISHMENTS: FIRST YEAR

The salient accomplishments of both the prior SSP/CCC project conducted by this investigator and the first nine months of the present project are summarized in the front section of this packet of materials. In addition, many findings of the prior project are described in detail in the supplemental papers attached as appendices to this report. Hence, this section will focus solely on the most significant details of the research performed thus far in the initial nine months of the current project.

II.A. Characterization of Aquifer Materials.

We obtained three types of samples for this project: two natural subsoil materials and an artificially coated sand. The two subsoils were collected by J. Zachara of PNL from the Milford sandpit in Delaware as part of a collection of materials planned for common use by SSP/CCC investigators. The Milford materials are micaceous silica sands from the Atlantic Coastal Plain chosen because they come from adjacent strata that are alternately well coated and lightly coated with iron oxides. Samples were drawn from both zones so that SSP/CCC researchers could compare two materials that differ primarily in the degree of a presumably adsorptive oxide coating. The samples here are termed Milford Coated and Milford Uncoated. Note however that the "uncoated" material possesses some Fe oxide coating and small but significant amounts of magnetite and hematite. The Milford Coated material has essentially no magnetite or distinct hematite and nearly all Fe in the material appears to be in the amorphous and weakly crystalline coatings. More complete mineralogical characterization is planned by PNL. For these experiments the subsoil samples were sieved to contain the fraction between 125 and 500 μm ; the use of a more uniform size fraction reduces variability among samples due to differences in the relative percentages of various size classes. Acid-washed polyester sieves were used to avoid the Fe contamination that metal sieves can create.

The third, synthetic sample, is a pure, uniform Ottawa sand that was artificially coated with amorphous Fe oxyhydroxides by immersion in a ferric chloride solution followed by base addition to precipitate the Fe. We do not believe this material accurately reflects the typical characteristics of a natural subsoil. However, the material is suspected to possess a relatively low degree of surface site heterogeneity.

Thus, this material is a simple porous matrix that will be used purely for certain comparison purposes.

Our laboratory has contributed to the collective knowledge base on these materials by performing isotherm titrations and pH edges for Cu, oxalate, and a Cu/oxalate mixture. These adsorption data satisfy our short-term modeling needs. In the near future we will perform acid-base titrations, and adsorption experiments for EDTA, Co(II), and Co(II)/EDTA mixtures.

II.B. Oxalate-Promoted Weathering: Batch Experiments

All three samples were exposed to a solution of 1 mM oxalate in a batch reaction system at pH 4. A large series of centrifuge tubes were prepared containing a 1:10 solid/liquid ratio. Tubes were mixed by very slow rotation in a 15°C constant temperature room. At regular intervals, replicate pairs of tubes were sacrificed and the solids removed after centrifugation to settle out the bulk particles and noncolloidal fines. Solids were washed in several changes of a pH 10 solution to desorb > 95% of adsorbed oxalate. The samples were then subjected to chemical "interrogation": oxalate adsorption isotherms along with pH edges for selected samples.

As expected, significant amounts of Fe and Al were released by the samples during the initial five-week (832 h) experiment. Of greater interest however are the observed changes in surface adsorption properties. Oxalate titration of the weathered materials reveal striking changes in surface properties over 832 h.

Fig. 1 shows the isotherms for the unweathered Milford Coated and the material as it appeared at the end of the experiment. Isotherms for the other materials showed very similar trends. The approximately one order of magnitude decline in the

Fig. 1. Oxalate adsorption isotherms for Milford Coated at pH 4, before and after weathering with 1 mM oxalate.

amount of sorptive capacity is evident across the entire isotherm. Less obvious in such a plot is the shift in the slope of the isotherm.

The isotherm of a material with a heterogeneous distribution of binding energies typically has a slope on a log-log plot that is less than unity. The slope of the unweathered Milford Coated in Fig. 1 is approx. 0.85. Note however that the weathering shifts the slope to near unity, suggesting the evolution of a more homogeneous surface. The results in Fig. 1 thus indicate that the loss of binding sites is not a simple removal of total capacity, but entails a narrowing of the range of binding energies. A logical assumption is that the high-energy binding sites are preferentially removed. Such a preferential removal is more easily detected if the data are plotted differently.

One way to visualize the strength of binding sites that control speciation at any point in the titration is to plot the log of the aqueous adsorbate conc. against the total adsorbate added to the system. In such a plot, a titration of an ideal "blank" yields a one-to-one mapping of free and total adsorbate. In the presence of an adsorbent surface, the values of free adsorbate plot below the blank or calibration line. The distance between the data points and the calibration line is proportional to the strength of the binding that is "locally" controlling the speciation of the adsorbate. Thus, a homogeneous surface yields data in a straight line, parallel to the calibration line (at least until site saturation is achieved). For a heterogeneous surface, the data will deviate the greatest at low total adsorbate, reflecting the small concentration of higher-energy binding sites. As total adsorbate is increased the strong sites are titrated, no longer control the speciation, and the data points gradually move closer to the calibration line.

A comparison of oxalate adsorption data for the unweathered and weathered Milford Coated shows exactly this difference (Fig. 2). The weathered material reveals a significant range of binding energies whereas the unweathered material is far more homogeneous.

Possibly the clearest way to visualize the loss of heterogeneity is to plot the apparent distribution coefficient throughout the adsorption titration as a function of total adsorbate added. The apparent K_d is simply the concentration of oxalate on the surface divided by the concentration in solution. At a given total oxalate conc., this

Fig. 2. Oxalate adsorption on Milford Coated at pH 4 presented in terms of aqueous speciation of oxalate; before and after weathering with 1 mM oxalate.

partitioning will be governed by the strength of the strongest sites that are not yet saturated by the adsorbate. Thus, for a homogenous material, the plot is simply a horizontal line. For a heterogenous material the data will show a high K_d at low total adsorbate, with the K_d dropping off as the strong sites are titrated (Fig. 3).

Fig.3 clearly shows the high heterogeneity of the unweathered material and the loss of this heterogeneity upon weathering. This plot also reveals the practical implications of this change in heterogeneity. Solid-liquid partitioning on the unweathered Milford Coated material greatly depends on the concentration of the adsorbate. A contaminant at very low concentration is strongly sorbed to the solid and has a correspondingly high retardation factor at equilibrium. A high concentration of contaminant will have a much lower overall partitioning and will exhibit a more mobile front. (For this reason, heterogenous adsorptive materials are said to produce "self-sharpening" solute fronts that do not spread out in proportion to the

distance advected). In contrast, well weathered material will exhibit nearly the same degree of partitioning at all concentrations; the solute fronts tend to move faster at low concentrations and to spread much more rapidly at all concentrations.

The general trends in adsorption characteristics presented here for Milford Coated were also observed for the other two materials, differing primarily in the exact values of coefficients.

II.C. Preliminary Modeling of the Evolution of Site Heterogeneity

The general features demonstrated by the batch experiments can be reproduced in a simple spreadsheet-based model of site alteration. As a first effort, we assumed a gaussian distribution of $\log K$ values for eight discrete site classes on a hypothetical heterogeneous adsorbent. Then, we assumed that the rate of dissolution of these

Fig. 3. Heterogeneity in the the binding of oxalate to Milford Coated at pH 4 as shown by the apparent K_d as a function of total oxalate added; before and after weathering with 1 mM oxalate.

sites is not equal but is proportional to the values of $\log K$. This assumption of a linear free energy relationship between binding energy and dissolution rate is hypothetical, but has a reasonable chemical basis; we will explicitly test this hypothesis with experiments in the coming year. We then began to "dissolve" the model surface by an iterative process and numerically sampled the adsorption characteristics at regular intervals. That is, we assumed a simple Langmuir model (typical for oxalate) for each site class and computed the overall isotherm that would be measured at each point in the dissolution process. The output, shown below for four arbitrary time intervals, were plotted in the three ways used for the experimental data above. These plots reproduce all the major features in the experimental data (Fig. 4). To this point the model has been used in a purely diagnostic mode to test whether it reproduces the characteristics of the evolving system. The next step is to optimize parameters to data for specific experiments. Although this model has too many adjustable parameters to be uniquely defined, it is a helpful mechanistic representation of a plausible process mechanism.

Fig. 4. Modeling results that predict the effect of the evolution of a hypothetical heterogeneous adsorptive surface. a. Predicted evolution of isotherms. b. Predicted evolution of solution speciation of adsorbate. c. Predicted evolution of apparent K_d as a function of total adsorbate (apparent site heterogeneity function).

II.D. Mini-Column Manifold

Batch experiments are useful and relatively simple, but even the most gentle mixing dislodges fines and colloids and may thereby cause unnatural changes in surface properties. Flow columns allow continuous washing of material without mechanical disturbance, but they must be dismantled to directly sample the solids.

We combined the flexibility of batch methods with the advantages of columns by constructing a manifold comprising 22 small (5 mL) "mini-columns" (Fig. 5). All mini-columns are exposed to a similar flow regime but each can be independently removed (or "sacrificed") for sampling. The system is highly useful for examining surface processes as a function of time. Because we are not using the mini-columns to investigate transport phenomena, the small size, wall effects, etc. are not significant problems. Multiple replicates are possible and the gravity-flow design ensures stability and reliability of operation for months at a time. The tubes are opaque PVC to exclude light and the entire apparatus runs in a cold room at 15°C.

Fig. 5. Schematic diagram of the mini-column manifold developed for subsoil weathering experiments.

In the current experiment the eluent is 1 mM oxalate at pH 4. The pH and concentration of Fe and Al are monitored in the effluent every 24 to 48 h. Total "exposure" of each mini-column is reckoned in terms of the number of pore volumes passed. The cumulative Fe and Al eluted for a current experiment are depicted in Fig. 6. Note that for Fe in Milford Coated the dissolution rate is fairly constant whereas for Al the overall rate gradually declines over time, suggesting a heterogeneous distribution of dissolution rates. Other soils show similar pattern. Adsorption analyses of sacrificed sample tubes are currently underway.

II.E. Column Experiments

Preliminary column experiments have recently been initiated. Four columns have been constructed and are currently in operation; the eluent is the same as in all other experiments to date (1 mM oxalate at pH 4). One column contains layers of all three materials to investigate systems with known heterogeneity at the REV scale.

These columns provide information complementary to that obtained from the manifold. In particular, the column studies will explicitly focus on changes in the transport properties of metal-ligand mixtures in a natural porous matrix undergoing geochemical surface evolution. A first evaluation of transport properties of the columns has been completed.

Breakthrough curves

for a conservative bromide tracer and a pulse of Cu-oxalate are shown in Fig. 7 below. The Cu is retarded relative to the Br, but the degree of retardation in this test is quite small because of the low pH and the presence of the oxalate chelator. We are evaluating the magnitude of retardation that would be optimal for interrogating the system and will make adjustments accordingly in the design of the pulse injections. However the preliminary experiments do indicate that the hydraulic behavior of the columns is satisfactory for our experimental goals.

III. PLANS FOR THE NEXT REPORTING PERIOD

III.A Synopsis of Planned Research Tasks

1. Further Documentation of Geochemical Evolution of Mineral Surfaces

Complete the experimental documentation of the ligand-promoted evolution of surface adsorption characteristics and site heterogeneity. Develop and test hypotheses on the mechanisms underlying the observed changes in the aquifer materials. Compare the utility of batch, mini-column, and full column methods.

2. Improved Modeling of Surface Heterogeneity

Test existing models of surface binding-site heterogeneity for their utility in modeling a dynamically evolving aquifer material. Collaborate with J. Westall (OSU) to investigate improved representations. Develop a robust and general chemical model of the dissolution of a heterogeneous mineral matrix

3. Transport Modeling of Column Experiments

Select an appropriate existing solute transport model that incorporates both equilibrium and kinetic adsorption/reaction processes. (KEMOD by G. Yeh et al. is the current candidate). Modify this code as needed to incorporate surface site heterogeneity and the evolution of surface sites over time. Apply the model in diagnostic mode to interpret processes observed in 1D column experiments.

4. Role of Natural Organic Matter in the Weathering/Evolution Process

Further investigation of the effects of natural organic matter (such as humates) on the mineral dissolution/surface-evolution process.

5. Extension to the EDTA/CoEDTA/FeEDTA System

Extend the current experiments to investigation of the CoEDTA system and its effect on surface heterogeneity. Collaborate with PNL researchers on preliminary column and 2D intermediate-scale flow cell experiments involving controlled heterogeneity at the REV scale.

6. Involvement with Future Field Site Experiments

Begin planning of collaborative involvement with SSP/CCC field site experiments currently in the planning stages. Examine field evidence/manifestations of evolving heterogeneity.

III.B. Specific Tasks for the Next Reporting Period

Compilation of Available Data. We believe that sufficient data is now available, either in the literature or through personal communications, about the single solute adsorption and solution-speciation properties of the target anions, at least for defined Fe oxides. We will initially create a critical compilation of thermodynamic data and SCM parameters for oxalate, EDTA, a well characterized soil humic acid extract prepared in this laboratory, and Co(II)EDTA complexes. Detailed information about the adsorptive properties of CoEDTA complexes will be drawn from the SSP/CCC research at Pacific Northwest Laboratories (PNL).

Competitive Adsorption Experiments. Our experience with oxalate and chromate has demonstrated that the adsorptive behavior of multi-component mixtures of anions must be experimentally determined. We will conduct a series of batch-type adsorption experiments with binary combinations of the target anions.

Note that an important property of oxalate and EDTA is that they all promote the dissolution of metal oxides. The explicit kinetic phenomena of these reactions will be explored in later stages, but these experiments focus strictly on equilibrium chemistry. As emphasized in the Background section, mineral dissolution does affect equilibrium speciation, but our extensive experience with oxalate/Fe oxide systems has shown that with proper controls, accurate equilibrium measurements can be made if $\text{pH} < 4$ is avoided, if careful tests of equilibrium stability are made, and if the experiments are completed on a time scale that is less than the time scale of significant mineral dissolution. To verify that kinetic processes are not interfering, some of the preliminary kinetic experiments described below will be conducted in parallel with these equilibrium studies.

Surface Complexation Modeling. The primary tool for modeling adsorption results will be the Diffuse Layer Model (DLM) which is a simple, but effective and well defined surface complexation model. We have used this model extensively in our laboratory (see Appendices A and B). In direct comparisons with the Triple Layer Model (TLM) we have found that the DLM works equally well and is a bit easier to parameterize (Appendix A). Our main goal is to have a consistent and effective modeling approach. However, we remain open to further evaluation of the TLM and other surface models as applied to these complex systems. All data will be fitted using the nonlinear parameterization program FITEQL in collaboration with J. Westall, OSU.

Ligand-Promoted Dissolution. Substantial literature data and data from this laboratory is available on the kinetics of the dissolution of Fe and Al oxides promoted by oxalate and EDTA. Other than a few experiments to "intercalibrate" our systems with the existing data, we are not replicating such studies but instead rely on the well established rate formulations for single-adsorbate experiments on well defined minerals. As above, we will create a critical compilation of dissolution rate parameters for the target ligands.

We will collaborate closely with the PNL group in this area to avoid duplication of effort. The PNL group has proposed experiments to examine the re-speciation of CoEDTA with Fe(III) liberated by this reaction. This phenomenon may affect our experiments so we will coordinate these experiments with the work at PNL.

Effect of Humic Matter on Dissolution. We are conducting oxalate-promoted dissolution experiments in the presence of soil humic acid. These experiments should yield some very interesting results because there is little comprehensive information in the literature about the effect of humic matter on ligand-promoted dissolution by small organic acids (P. Maurice-Johnsson, pers. comm.) As described above, uncertainty in the mechanism of humate binding to mineral surfaces precludes a general prediction of humic acid on oxalate-promoted dissolution so the role of humic acids is still poorly understood.

Dissolution of Natural Fe Oxides. An important set of experiments focuses on the rate of ligand-promoted dissolution of naturally heterogeneous Fe-oxide minerals. For these systems we are using a "mini-column manifold" so that relatively long contact times can be maintained without a commensurate build-up of dissolved Fe in the system. The manifold apparatus is depicted in the Scientific Progress section that follows. Briefly, a set of 22 small "mini-columns" are connected to a manifold that delivers an eluent solution at constant hydraulic head. Each mini-column contains about 5 g of subsoil sample. All samples are simultaneously exposed to the same eluant (1 mM oxalate in 0.05 M background electrolyte) and approximately the same flow regime but each sample can be independently removed from the manifold for analysis. This method allows us to maintain a relatively constant solution composition over long sequence of mineral dissolution. This set-up also more closely approximates the continuous-flow conditions in an aquifer than does a simple batch reactor. Also, the method substantially reduces the disruption and mobilization of fines and colloids, a serious problem in even gently mixed batch systems.

During the elution process, the pH and concentration of dissolved Fe and Al are monitored in the effluent. The total volume of eluant is also monitored as a function of time. After mineral samples have been extensively "weathered" in this process, we remove samples at set intervals, wash each several times to desorb remaining ligands, resuspend the sample, and use it to repeat some of the binary adsorbate equilibrium experiments that previously revealed the degree of competitive surface interactions.

Column Studies of Solute Transport. Because the ultimate goal of this research is to understand the impact of the weathering or surface evolution process on contaminant transport, we are conducting 1D flow-column experiments. Soil samples are packed into 20 cm x 5 cm polyacrylate columns, using standard procedures. Columns are eluted with the oxalate solution described above fed from a peristaltic pump and monitored as with the mini-columns. Whereas the mini-columns are simply sacrificed sequentially for analysis over time, the larger columns are "interrogated" periodically by the injection of adsorbate solutions. In the initial experiments, the columns are eluted for two weeks and then once per

week a pulse of Cu^{2+} (or Cu-oxalate complex) is injected. Cu is an easily analyzed transition metal that adsorbs (apparently as the Cu-oxalate⁺ complex) to the matrix material. The corresponding breakthrough curve reveals information about the average strength of binding in the system as well as kinetic (nonequilibrium) effects. Subsequent experiments will employ EDTA as an eluent and CoEDTA as the interrogating adsorbate. The metal breakthrough data are analyzed in the context of batch isotherms performed on samples taken from the mini-column manifold. The combined data allows us to draw a fairly complete picture of the surface complexation state of the matrix at any point during the weathering process. We have found that this combination of experimental methods is necessary to fully document the geochemical evolution and its effect on transport.

Numerical Modeling. As discussed above, an existing numerical model, such as KEMOD (developed by G. Yeh and co-workers at Penn State) will be the basis for modeling the phenomena observed in the column experiments. KEMOD appears to be a good choice because it efficiently accounts for both equilibrium and nonequilibrium adsorption. KEMOD is being modified by J. Szecsody at PNL to incorporate more extensive kinetic phenomena related to the Co/Fe exchange reactions in the PNL experiments. We anticipate that KEMOD will be satisfactory for interpreting the breakthrough curves of the column experiments; for example, interpreting the relative role of kinetic and equilibrium processes. Other data analyses, such as moment analysis of the breakthrough curves, will be explored in collaboration with A. Valocchi, (U. Illinois). We also will explore the feasibility and utility of modifying the transport code to allow it to account for a slowly evolving set of surface parameters.