Development of Modeling Methods and Tools for Predicting Coupled Reactive Transport Processes in Porous Media at Multiple Scales

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OBJECTIVES

The objectives of our present project are: 1) to develop numerical and analytical modeling approaches and simulation tools that can predict the transport of DOE-relevant contaminants [a metalloid, oxyanion [As(III/V)] and radioactive cation [U(VI)]] in subsurface systems, 2) to study the interactions of these contaminants with synthetic subsurface media under well-controlled conditions across a range of scales from laboratory batch to one dimensional soil columns to two-dimensional soil box experiments, and 3) to investigate the scaling issues inherent in the interactions of these contaminants with different types of subsurface materials.

MODEL DEVELOPMENT

NUMERICAL

Our numerical effort focuses on developing a new version of the DOE's reactive transport model RT3D. Figure 1 shows a summary of various components of the code development effort. We have coupled a surface-complexation module used by MINTEQ within RT3D to predict reactive transport processes coupled to surface-complexation reactions. A version of this code is currently being implemented to run in a parallel-processing mode within a multi-processor Pentium platform.

ANALYTICAL

General closed form solution to multi-species reactive transport equations that are coupled through sorption and radioactive decay reactions will be useful to predict the long-term transport of radio nuclides. We have derived a closed-form analytical solution to this problem for spatially-varying initial conditions. Two distinct solutions are derived to support Dirichlet and Cauchy boundary conditions, each with Bateman-type source terms. The new solution procedure employs a combination of Laplace and linear transform methods to uncouple and solve the system of partial differential equations. We have organized the final solution in a general format that represents the solutions to various boundary and initial conditions. Figure 2. shows the summary of the transport equations solved and the solution methods used in this analysis.

EXPERIMENTAL METHODOLOGY

Goethite coated sand (GCS) were synthesized by reported methods (Schwertmann and Cornell, 2000; Scheidegger et al., 1993). Morphological analysis of the GCS was performed by scanning electron microscopy (SEM). The goethite and GCS were characterized by X-ray diffraction, Fourier transform infrared spectroscopy. The crystalline and amorphous iron were quantified using dithionate-citrate-bicarbonate (DCB) and AOD (ammonium oxalate extraction in dark) methods. The specific surface area was measured using multipoint BET method.

Batch adsorption of As (As(III) & As(V)) or U(VI) were studied using reactors containing fixed amount of GCS (1-100 gL⁻¹). Adsorption isotherms were produced by varying the As or U(VI) initial concentration at a fixed pH. The adsorption envelopes were generated with a fixed As or U(VI) concentration (1 mg L⁻¹) and varying the pH. Reactions proceeded for 24 h (for As) and 48 h (for U(VI) at 22° C in a shaker at 200 rpm. After equilibrium, the supernatant solution was filtered and analyzed by graphite furnace atomic absorption spectrophotometer (GFAAS; Perkin-Elmer 3110 PC) for As and kinetic phosphorescence analyzer for U(VI).

Sequential batch reactions (SBR) were conducted using three batch reactors in series. Two reactor volumes of As(V) solution progressed through three reactors sequentially, after equilibrium in each reactor. Two reactor volumes of background solution followed in the same manner in order to investigate desorption. The solutions were filtered and analyzed upon removal from the final reactor by GFAAS. The surface complexation models (SCM) were used to design transport experiments.
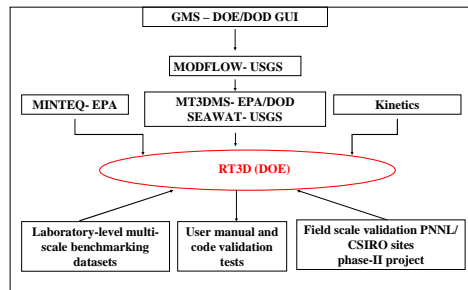
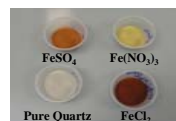## SYNTHESIS AND CHARACTERIZATION

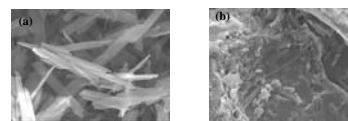**Figure 2. Goethite-coated sand from various systems**

**Figure 3. (a) SEM image of goethite from heterogeneous system; (b) GCS from homogeneous system after DCB extraction**

Figure 1. Numerical modeling framework.

EXAMPLE OF 4 MEMBER DECAY CHAIN

Parent-1 → Daughter-2 → Grand daughter-3 → GGD-4 …

$$[R]\frac{\partial}{\partial t}\{c\} + v\frac{\partial}{\partial x}\{c\} - D_x\frac{\partial^2}{\partial x^2}\{c\} - D_y\frac{\partial^2}{\partial y^2}\{c\} - D_z\frac{\partial^2}{\partial z^2}\{c\} = [YK]\{c\}$$

$$c_i(x,t) = \sum_{i_1=1}^{i}\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_3=i_1}^{i}\sum_{i_4=i_3}^{i_5}\{G_1^1 + h(G_1^1)\ G_2^1\}$$
$$+ \sum_{i_1=1}^{i}\left[R_{i_1}c_{i_1}^o\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\{G_1^2 + h(G_1^2)G_2^2\}\right]$$
$$; \ \forall\ i = 1, 2, \dots n$$

Figure 2. Analytical modeling framework.

EXPERIMENTAL AND MODEL RESULTS
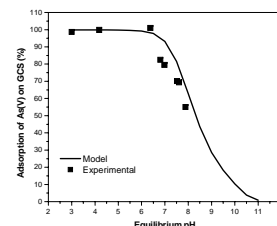
Figure 4. Adsorption of As(V) on GCS as a function of pH.
The SCM reaction equations are given in Table 1.

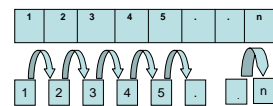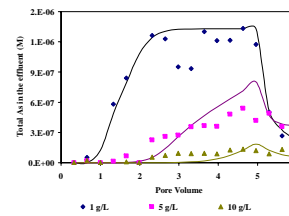| Protonation reactions for As(V)		
H_3AsO_4	$- H^+$	$= H_2AsO_4^-$
H_3AsO_4	$-2 H^+$	$= HAsO_4^{2-}$
H_3AsO_4	$-3 H^+$	$= AsO_4^{3-}$
Acid/ Base reactions of goethite-coated sand		
$>FeOH$	$+ H+$	$> FeOH_2$
$>FeOH$	$- H+$	$> FeO^-$
As(V) surface complexation reactions		
$>FeOH$	$+H_3AsO_4$	$= >FeH_2AsO_4 + H_2O$
$>FeOH$	$+H_3AsO_4 - H+$	$= >FeH_2AsO_4^- + H_2O$
$>FeOH$	$+H_3AsO_4 - 2H+$	$= >FeH_2AsO_4^{2-} + H_2O$

Table 1. SCM reaction equations

Figure 5. Transport and adsorption of 0.1 mgL⁻¹As(V) on GCS through three sequential batch reactors. Model results were generated using PHREEQC.

- A diffuse double layer model was used to predict As(V) adsorption onto GCS using one type of surface sites. The equilibrium constants for the surface complexation of As(V) on goethite were determined using FITEQL 4.0 (Table 1) and the results are shown in Figures 4 and 5.
- In the case of uranium, when the adsorption of U(VI) onto all GCS were normalized to their iron content similar pattern was observed (Fig. 6).
- The surface complexation model (SCM) developed for the predicting the sorption of U(VI) to hydrous ferric oxide (HFO) by Waite et al. (1994) was used to model the above system.
- The model appears to over predict the experimental results (Fig. 7). This might be due to the differences in the surface area of HFO and goethite. Also the surface complexation constants we used in the model was based on U(VI) sorption to amorphous HFO, not for crystalline goethite; this could have influenced our model results.
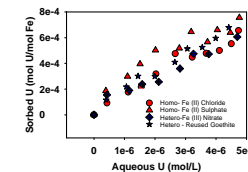

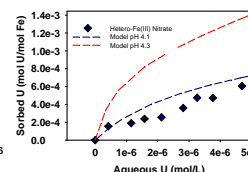**Figure 6. Adsorption of U(VI) to GCS after normalizing to iron content**

Figure 7. Adsorption of U(VI) to GCS in comparison with SCM model prediction

ANALYSIS OF DENSITY DRIVEN REACTIVE FLOWS

Nuclear wastes disposed at DOE sites are mostly mixed with multiple co-contaminants that considerably increase the overall density of the waste. One of the objectives of this project is to generate well-controlled experimental datasets to visualize density driven, two-dimensional reactive flows and explore methods to scale these flows. Figure 8 shows the movement of dense (saltwater) plume in a freshwater system under various ambient groundwater flow conditions. These laboratory dataset indicates that high ambient flow will lead to a stable plume condition where the dense water is transported through a narrow region above the less dense fluid. On the other hand, reduced groundwater flow conditions can lead to sinking plumes that rapidly contaminate large volumes of groundwater. In addition, the mixing between fresh and dense waters is high under low flow conditions. Since the reaction rates are proportional to the level of mixing, one can expect low flow conditions to favor strong chemical interactions between ambient groundwater and anthropogenic wastewater.
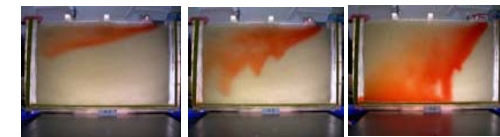

Figure 8. Density driven reactive flow under high, medium, and low GW flow

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