

Modeling Fate and Transport of Inorganic-Organic Co-Contaminants at a DOE Fractured Waste Site

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1 ABSTRACT

The objective of the research is to study the effects of physical and chemical heterogeneities at matrix block and field scales on the fate and transport of Co(II)EDTA at a DOE low-level waste disposal site at Oak Ridge National Laboratory (ORNL). The field site, Waste Area Grouping 5 (WAG 5), is highly heterogeneous with confined, fractured aquifers and partially weathered shale bedrocks and saprolite near ground surface. Laboratory experiments using undisturbed saprolite soil columns and field experiments using multiple reactive and non-reactive tracers have been conducted to elucidate mechanisms governing the fate and transport of metal and metal-EDTA chelates such as Cr, Co(II)EDTA, CdEDTA and non-reactive tracers such as Br, He, and Ne. Laboratory observations from Co(II)EDTA injection into a saprolite soil was used to calibrate a two-pore-domain, fracture-matrix reactive transport model. The goal of the study is to determine mass transfer and transport parameters and kinetic reaction rate coefficients that characterize physical and chemical non-equilibrium, respectively, at matrix block scale. Model parameters thus obtained were then used for a field scale transect model of WAG 5 to study the effect of field scale heterogeneity on the fate and transport of Co(II)EDTA. The field scale model was first calibrated hydraulically using field observations of groundwater levels at monitoring wells installed along the transect. Tracer breakthrough curves at these wells were then used to calibrate a two-pore-domain model for the transport of non-reactive tracers (Br and Ne). The latter modeling effort was designed to study the effects of physical non-equilibrium on field scale transport of non-reactive tracers. Finally, sensitivity analysis is conducted to study the effects of physical and chemical heterogeneities on the fate and transport of Co(II)EDTA at field scale.

2 INTRODUCTION

Matrix diffusion is a widely observed phenomenon in fractured porous medium (e.g., Neretnieks, 1980; Novakowski and Lapcevic, 1994; Jardine et al., 1999). It is a comparatively small-scale effect that has also been observed to have effects on field scale movement of solutes (e.g., Jardine et al., 1999). Previous modeling studies of fate and transport in fractured geological formations include equivalent porous medium (e.g., Lee et al., 1992; Allen and Michel, 1999; Bodvarsson et al., 2003), discrete single or multiple fractures of various shapes and connectivity (e.g., Sudicky and McLaren, 1992; Tsang and Tsang, 1987), and models consisting of two or more interactive pore domains (e.g., Gerke and van Genuchten, 1993; Gwo et al., 1996). These models and their computational counterparts, from simplistic to complex, have various degrees of utility as more and more information of the subsurface is gathered. However, large uncertainty may exist because it is often impractical to characterize experimentally field scale heterogeneities at matrix block scale (Gwo et al., 2004b). For reactive transport of metal and metal-chelates, this observation is further complicated by the lack of information in solid surface properties that may vary from pore domain to pore domain

and from formation to formation. As a result, characterization and remediation of contaminated field sites may require more extensive, and often times more expensive, data collection and analysis efforts. Sensitivity and cost-benefit analyses may also be necessary to address the issues of characterizing physicochemical heterogeneity, prioritizing data collection efforts and managing monetary risks of various remediation designs (e.g., James et al., 1996).

The objective of the research is to study the effects of physical and chemical heterogeneities at matrix block and field scales on the fate and transport of Co(II)EDTA at fractured waste sites. A multiscale approach involving laboratory and field injections of Co(II)EDTA into undisturbed saprolite soil column and fractured formations at the WAG 5 site, respectively, is used. Reactive transport model parameters obtained from the calibration of a soil column model are used in sensitivity analysis for a field scale, transect model of WAG 5. The goal is multifold: (1) determine the most sensitivity parameters for field scale model calibration effort using field observations of reactive tracer injection (Jardine et al., 2002), (2) determine the relative effects of physical and chemical mass transfer, and (3) determine the most relevant scales of various physicochemical processes.

3 METHODOLOGY

A transect of one source well, two multilevel monitoring wells, and 20 clusters of drive-point wells were installed at the WAG 5 site (Figure 1). Non-reactive tracers, metal and metal-EDTA chelates were released in two successive experiments at the source well. Bromide, helium and neon were released in the first experiment to study the effect of matrix diffusion on field scale transport and to characterize physical non-equilibrium as a result of tracer movement between pore domains or fracture and matrix. Metal and metal-EDTA chelates were released in the second experiment to study their fate and transport in highly structured soils and geological formations. Groundwater levels and movements of the chemicals were monitored through the multilevel and drive-point wells. Undisturbed soil columns were collected from soil horizon C, mostly saprolite that is partially weathered shale bedrock and may have retained the majority of the physical and chemical properties of the bedrock. Co(II)EDTA tracer injection was conducted in the laboratory using the undisturbed soil columns.

A two-pore-domain, fracture-matrix groundwater flow model is calibrated using observed groundwater level and a multiple-pore-domain flow simulator MURF (Gwo et al., 1994; Gwo et al., 2004a). Flow fields in the fracture and matrix pore domains thus calculated are used to calibrate a non-reactive transport model of Br and He release at WAG 5 (Gwo et al., 2004b), using the tracer release data and a multiple-pore-domain

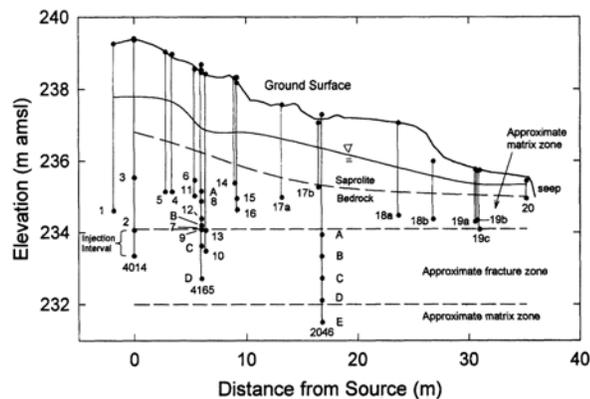


Figure 1. ORNL WAG 5 transect and wells.

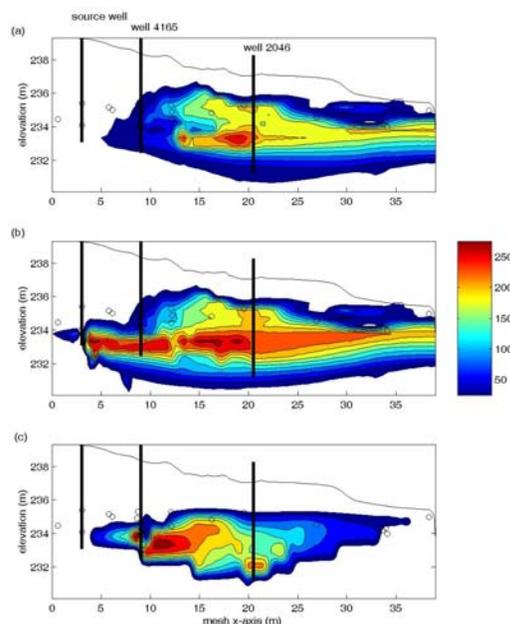


Figure 2. Observed Br concentration (c) and those calculated in fracture and matrix (a and b, respectively).

transport simulator MURT (Gwo et al., 1995; Gwo et al., 2004b). The purpose of the calibration efforts is to determine advective and diffusive mass transfer coefficients that characterize physical non-equilibrium as results of pressure and concentration differences between pore domains, in addition to determining field scale heterogeneities that are responsible for preferential flow and transport of fluids and solutes. Shown in Figure 2 are the calculated Br plumes in the fracture and matrix (panels a and b) and the observed Br plume (panel c).

4 RESULTS AND DISCUSSION

A network of interfacial reactions were used to represent the surface MnO_2 mediated transformation of $Co(II)EDTA$ to $Co(III)EDTA$. Laboratory observations are used to determine kinetic reaction rate coefficients for the oxidation of $Co(II)EDTA$ to $Co(III)EDTA$ by surface MnO_2 , by fitting model predictions to observed soil column tracer breakthrough curves (Figure 3). The results indicate that both physical and chemical mass transfer processes may affect the adsorption and movement of $CoEDTA$ in structured soils.

The reaction network, the kinetic rate coefficients obtained from the soil column modeling exercise and the physical mass transfer coefficients obtained from the field scale model of non-reactive tracer transport are subsequently used in modeling field scale fate and transport of $Co(II)EDTA$. Large scale heterogeneities, including matrix and fracture characteristic length, porosity, dispersivity, tortuosity and flow fields of pore domains obtained from previous flow and non-reactive solute transport model calibrations are used in conjunction

with the soil column modeling results to conduct sensitivity analysis. Shown in Figure 4 are the concentrations of $Co(II)EDTA$ in the fracture and matrix. Because the movement of $Co(II)EDTA$ in the matrix is relatively slower than that in the fracture, the majority of $Co(II)EDTA$ in the matrix, except the area near the source well (red oval near the left boundary), is a result of physical mass transfer. Nonetheless, the distribution of $Co(II)EDTA$ between the aqueous and solid phases in the fracture domain (Figure 5) suggests that, at field scale, chemical mass transfer may have a more profound impact relative to physical mass transfer on the transport of $Co(II)EDTA$. Note that both figures show calculations at approximately 20 hours since the release of $Co(II)EDTA$ was started. $Co(II)EDTA$, once absorbed on solid surface, undergoes a quick transformation, mediated by MnO_2 , to

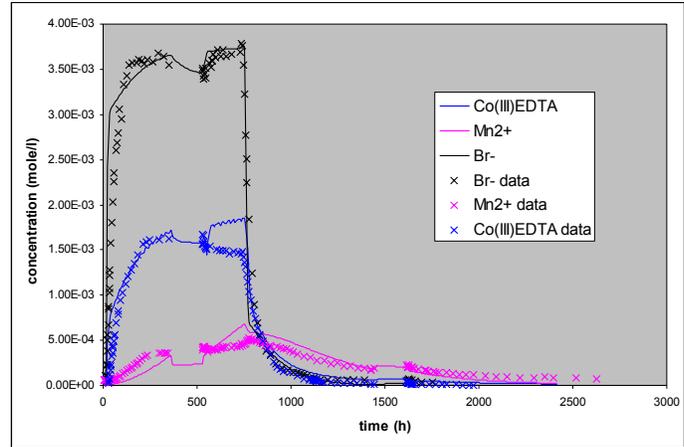


Figure 3. Predicted and observed reactive tracer breakthrough curves.

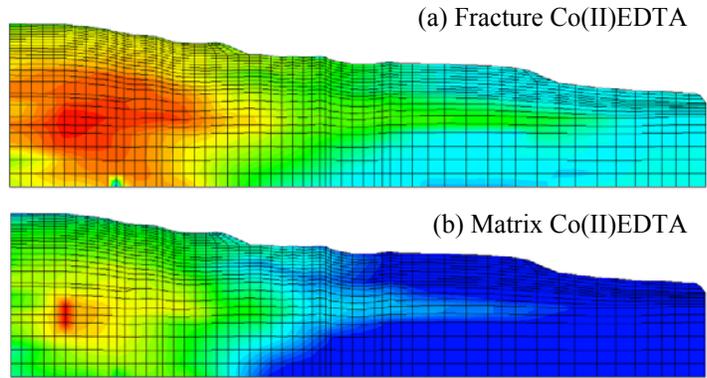


Figure 4. Predicted $Co(II)EDTA$ concentrations in the (a) fracture and (b) matrix. Note that concentrations are plotted in logarithmic scale.

Co(III)EDTA. As a result, surface MnO_2 is quickly consumed near the source area. Downstream from the source area, aqueous free Mn and adsorbed Mn concentration steadily increase as upstream MnO_2 is dissolved (data not shown). Note that the spatial distribution of surface MnO_2 is assumed uniform initially over the entire transect. As of the writing of the paper, effort is underway to incorporate chemical heterogeneity in the WAG 5 model and to study the effect of spatial variation in MnO_2 on the fate and transport of Co(II)EDTA.

5 ACKNOWLEDGEMENT

The authors are greatly indebted to the financial support of Dr. Paul Bayer in the DOE Environmental Technology Partnership Program.

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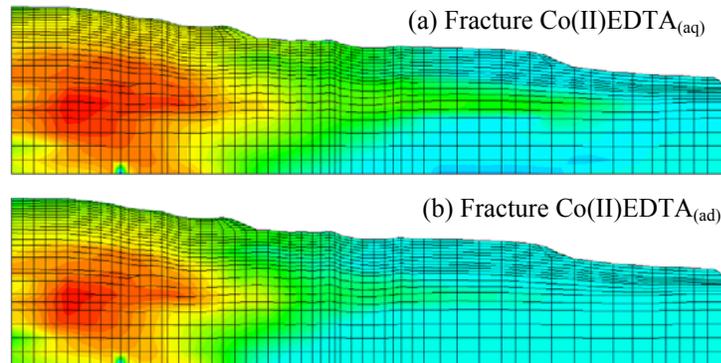


Figure 5. Predicted Co(II)EDTA concentrations in the (a) aqueous and (b) solid phases in the fracture. Note that concentrations are plotted in logarithmic scale.