

# Modeling U(VI) Biomineralization in Single and Dual Porosity Porous Media

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## **Abstract**

Uranium extraction, processing and storage have resulted in a legacy of uranium-contaminated groundwater aquifers worldwide. An emerging remediation technology for such sites is the in situ immobilization of uranium via biostimulation of dissimilatory metal reducing bacteria (DMRB). While this approach has been successfully demonstrated in experimental studies, advances in understanding and optimization of the technique are needed. The motivation of this work was to understand better how dual-porosity (DP) porous media may affect immobilization efficiency via interactions with the dominant geochemical and microbial processes. A biogeochemical reactive transport model was developed for uranium immobilization by DMRB in both single and DP porous media. The impact that microbial residence location has on the success of biostimulated U(VI) immobilization in DP porous media was explored under various porosity and mass transfer conditions. Simulations suggest that DP media are likely to show delayed U(VI) immobilization relative to single porosity systems. U(VI) immobilization is predicted to be less when microbial activity is restricted to diffusion-dominant regions but not when restricted to advective-dominant regions. The results further highlight the importance of characterizing the bioresidency status of field sites if biogeochemical models are to predict accurately remediation schemes in physically heterogeneous media.

*Keywords:* remediation, uranium, reactive transport, subsurface, model, dissimilatory metal reducing bacteria

# 1 Introduction

Uranium extraction, processing and storage have resulted in a legacy of uranium-contaminated groundwater aquifers. Leaching from poorly designed storage facilities and mill tailings is of serious environmental concern [Riley *et al.*, 1992; Landa and Gray, 1995]. In natural waters, uranium in its oxidized U(VI) state commonly forms stable aqueous complexes (e.g., carbonate, hydroxide) of high solubility and mobility [Langmuir, 1978], and is potentially toxic over long periods ( $^{238}\text{U}$  half life is  $4.5 \times 10^9$  y).

Radionuclide-contaminated land remediation strategies that involve excavation are often expensive, impractical (due to the large volumes of material), and potentially hazardous. Capture and control strategies, using a pump-and-treat approach, do not solve the source of the problem and thus can be expensive in the long term. In situ bioremediation approaches present an attractive alternative, particularly for dispersed contaminant plumes over large areas and/or at great depth, and may be more cost effective [Macaskie *et al.*, 1997; Quinton *et al.*, 1997; Lovley and Philips, 1992b]. Bioremediation causes reduction of U(VI) to the reduced U(IV) state, in which the uranium is typically present as immobile uraninite ( $\text{UO}_2$ ), a mineral of low solubility [Langmuir, 1978; Lovley *et al.*, 1991]. The remediation approach thereby reduces uranium migration in subsurface environments by precipitating and immobilizing it [Abdelouas *et al.*, 1998, 2000; Senko *et al.*, 2002; Anderson *et al.*, 2003].

The study of dissimilatory metal reducing bacteria (DMRB) has received increased interest [e.g., Gorby and Lovley, 1992; Lovley and Phillips, 1992a; Lovley *et al.*, 1991; Ahmann *et al.*, 1994; Oremland *et al.*, 1994; Lovley, 1995] due to the bacteria's

ability to carry out this reductive process [Lovley and Phillips, 1992a,b]. DMRB use naturally present Fe(III) and Mn(IV) oxides in aquifers as terminal electron acceptors (EAs) for their growth and maintenance [Wilson *et al.*, 1993]. The ability of Fe(III)- and sulfate-reducing organisms to reduce U(VI) enzymatically in laboratory cultures has been studied relatively intensively [e.g., Lovley *et al.*, 1991; Lovley and Phillips, 1992a, b; Gorby and Lovley, 1992; Lovley, 1993; Caccavo *et al.*, 1994; Lloyd and Macaskie, 1996; Gorby *et al.*, 1998; Tebo and Obraztsova, 1998; Lloyd *et al.*, 2000; Chang, 2005]. Stimulation of U(VI)-reducing bacteria by addition of an electron donor (ED) has also proved successful both in the laboratory [Truex *et al.*, 1997; Fredrickson *et al.*, 2000; Liu *et al.*, 2002; Gu and Chen, 2003; Suzuki *et al.*, 2003] and in situ [Abdelouas *et al.*, 1998, 2000; Senko *et al.*, 2002; Anderson *et al.*, 2003]. Furthermore, DMRB appear to be ubiquitous and indigenous to the natural environment [Abdelouas *et al.*, 2000; Snoeyenbos-West *et al.*, 2000; Petrie *et al.*, 2003; North *et al.*, 2004], making their exploitation an attractive in situ bioremediation option.

The processes involved in such systems are complicated and not yet fully understood. The interactions between geochemical, biological and physical processes are expected to be critical, particularly for highly heterogeneous and structured porous media. Contrasting zones of low- and high- hydraulic conductivity (K), including fractured rock and clay or disjointed sub-domains (e.g., lenses) can provide preferential flow paths and interconnected networks characterized by both high- and low-permeability material. In such environments, transfer of contaminants and injected fluids (e.g., ED) into aquifer sub-domains may occur because of diffusion from high-K to low-K zones. Thus, physically structured media may significantly

affect bioremediation efficiency either through DMRB accessibility to the ED or contaminant [Luo *et al.*, 2005; Roden and Scheibe, 2005; North *et al.*, 2004] or by inducing microbial or mineralogical heterogeneity [Vrionis *et al.*, 2005; Nyman *et al.*, 2006].

More recently, numerical models targeted at simulating these systems have been developed in an attempt to gain better understanding of the complex interaction between the biological, geochemical and solute transport processes involved [Wang and Papenguth, 2001; Wang *et al.*, 2003; Roden and Scheibe, 2005; Luo *et al.*, 2007]. A few of these studies account for the heterogeneous physical structure of aquifer porous media by modeling solute transport using a multi- region or porosity approach. This approach is widely accepted for the modeling of media which possess local flow variations and interregional diffusion due to the existence of fractures, contrasting zones of low- and high- hydraulic conductivity, and/or preferential flow paths [Feehley *et al.*, 2000; Haws *et al.*, 2004; 2005]. A multi-porosity approach involves characterization of the media by two or more overlapping flow continua [e.g. van Genuchten and Wierenga, 1976; Haws *et al.*, 2004; Jørgensen *et al.*, 2004]. In a dual-porosity approach a “mobile” region is conceptualized as exhibiting a relatively high-velocity range transport behavior dominated by interregional diffusive mass transfer, while a second “immobile” region is conceptualized as exhibiting a contrastingly low-velocity range transport behavior. Modeling systems with heterogeneous hydraulic conductivity using the two-region approach has successfully reproduced observed solute transport behavior [e.g. Li *et al.*, 1994; Bajracharya and Barry, 1997; Feehley *et al.*, 2000].

The multi-porosity biological models must consider in which region(s) microbial activity occurs. Unfortunately, there are very limited data that identify the residential preferences of microbes in subsurface porous media, especially under remediation schemes. The available data are further distorted by the act of gathering the media, the method of analysis, and the choice of sample media [Lehman *et al.*, 2004].

Subsurface studies have found microbial activity correlated with porosity [Musslewhite *et al.*, 2003], media type [Madsen and Ghiorse, 1993] and grain size [Kieft *et al.*, 1995]. However, as each of these characteristics may be correlated with one another, it is not possible to generalize any association between microbial activity and such characteristics. It is likely that organic carbon (OC) and ED presence are the most significant control over microbial presence in media regions. Indeed, the undisturbed subsurface has shown microbial activity correlated with higher carbon contents [Kieft *et al.*, 1995]. Deep aquifers have also shown OC fermentation restricted to the clayey confining sediment [Lovley and Chapelle, 1995] in which OC may be detained. Nevertheless, the dominant subsurface bacterial activity may instead take place at the interface between different media/porosity regions [Detmers *et al.*, 2001; Ulrich *et al.*, 1998]; for example, at a sandstone-shale interface [Krumholz *et al.*, 1997]. It is often assumed that this is due to diffusion of existing EDs from fine-grained, organic-rich higher-porosity sediments to other regions. However, in bioremediation schemes in which OC is injected into the subsurface, the initial natural ED content may become less significant to the microbial distribution: bacterial communities may instead favor the more mobile (higher hydraulic conductivity) regions where (injected) ED concentrations are higher and therefore more accessible to the bacteria.

Furthermore, bacterial growth or movement may be restricted by porous media physical conditions. Porosity networks with pore throat sizes narrower than the bacterial cell diameter prevent bacterial penetration into these regions [*Fredrickson et al.*, 1997]. Porous media regions in which EAs or EDs are diffusion-limited or that are experiencing biomass sloughing due to rapid flow-induced shear forces [*Applegate and Bryers*, 1991] may be less likely to harbor significant bacterial populations. *Roden and Scheibe* [2005] chose to model DMRB presence in only the diffusive mid-region of their tri-region model, in part for the above reasons.

Such varied data and conditions make it difficult to generalize how characteristic regional media conditions and microbial residence are linked. Many authors consequently assume that (i) all biological processes are restricted to a chosen region(s) [e.g. *Roden and Scheibe*, 2005], or (ii) bioactivity occurs in all regions [e.g. *Luo et al.*, 2007]. It is not known what effect such assumptions have on the outcome of modeling calculations. Moreover, the effect of such assumptions may influence field site characterization decisions.

The aim of this work is to give preliminary insight into the specific effects dual porosity (DP) porous media might have on U(VI) bioremediation efficiency. This is explored via developing a reactive transport model that accounts for the physical processes in such geological media as well as relevant geochemical and biological processes, including complex U(VI) desorption/sorption behavior and multiple terminal electron accepting (TEA) processes. Details of the model development and relevant literature are presented, followed by a comparison to an existing model for a

single porosity (SP) porous medium simulation. Simulations examining model predictions for DP porous media are then considered. In addition, sensitivity simulations explore the influence of porosity ratio, inter-region mass transfer rate, and bacterial residence location.



## **2 Theoretical background and model development**

A numerical model for biomineralization of U(VI) by DMRB is developed here in order to explore the efficiency of U(VI) remediation by DMRB in porous media exhibiting both single and DP behavior. The model is built in the USGS package PHREEQC [Parkhurst and Appelo, 1999] and couples 1D advective-dispersive solute transport with the complete set of aqueous speciation, precipitation/dissolution and primary and secondary redox reactions included in the MINTQA2 4.00 chemical database [Allison *et al.*, 1991]. A flow path (one-dimensional) system is considered in this work, providing an appropriate first step towards simulating and understanding such complex systems.

### **2.1 Biogeochemical model**

#### **2.1.1. Partial Equilibrium Approach**

Subsurface microbial metabolism generally consists of a two-step process involving inorganic redox chemistry and organic carbon oxidation [e.g., Lovley and Phillips, 1988; McMahon and Chapelle, 1991; Chapelle and Lovley, 1992; Murphy *et al.*, 1992; Robertson *et al.*, 1996]. Microbes in subsurface environments act as catalysts by mediating the electron transfers necessary for redox reactions. In doing so they obtain a source of energy required for their maintenance and growth.

The first of the two steps is the fermentation of dissolved organic carbon (DOC) which yields products such as acetate, formate and H<sub>2</sub>. The fermentation products are consumed as EAs by different TEA processes. Since the energy yield from the fermentation step is relatively small, the differences in energy yield largely result from the second TEA step [Postma and Jakobsen, 1996]. It is generally accepted that

the net reaction is rate-limited by the fermentation step [e.g., *Berner*, 1980; *Westrich and Berner*, 1984; *Middelburg*, 1989; *Boudreau and Ruddick*, 1991]. This is supported by the brief presence and low concentrations of the intermediate fermentation products, suggesting that the TEA step is much faster than the fermenting step. Of the two steps in each net reaction, fermentation is therefore considered to be rate-limiting, implying that the net reaction kinetics cannot be determined by the net energy yield. Rather, the first fermentation step is defined kinetically, and the path of the second TEA step is determined by chemical equilibrium (the energy yield of the TEA step) [*Postma and Jakobsen*, 1996]. It should be noted that this approach may be inappropriate for modeling processes in which the TEA step is rate limiting, as is possible in, for example, the case of dissimilatory iron reduction [*Liu et al.*, 2001]. In such cases, the redox zonation of the system may be different.

The individual TEA processes are considered to occur in a sequence determined by their Gibbs free energy yield [e.g., *Berner*, 1981a; *Stumm and Morgan*, 1981], with the widely accepted TEA processes sequence itself based on the work of *Baedecker and Back* [1979a,b], *Champ et al.* [1979] and *Nicholson et al.* [1983]. The resulting spatial and temporal segregation of the different TEA processes during degradation of organic matter in sediments, referred to as redox zonation, tends to follow this accepted sequence of TEA processes. However, the accepted sequence is a simplified and idealized representation of redox zonation. In reality, redox zonation may be affected by a variety of hydrological and geochemical phenomena resulting in the overlap of different redox zones, allowing multiple TEA processes to occur simultaneously, although one particular redox process may dominate. This overlap of

simultaneous redox reactions has been observed at field sites [e.g., *Berner*, 1981b; *Lovley and Goodwin*, 1988; *Kuivila et al.*, 1989; *Parkes et al.*, 1990; *Canfield et al.*, 1993; *Wersin et al.*, 1993; *Postma and Jakobsen*, 1996; *Jakobsen and Postma*, 1999].

To account for the fact that TEA processes are driven by a kinetic first step and a chemical equilibrium second step, *Postma and Jakobsen* [1996] recommended use of a Partial Equilibrium Approach (PEA) model. The PEA modeling method was proposed by *McNab and Narasimhan* [1994] and was further used by, amongst others, *McNab and Narasimhan* [1995], *van Breukelen et al.* [1998], *Keating and Bahr* [1998], *Jakobsen and Postma* [1999], *Prommer et al.* [1999a,b] and *Brun et al.* [2002]. The oxidation of organic matter (fermentation) is assumed to be the rate-controlling step and is represented by a kinetically controlled release of zero-valent carbon into solution. The second (equilibrium) step, controlling the sequence of TEA processes, occurs instantaneously. This approach allows for simultaneous redox reactions, without violation of thermodynamic laws, and for the straightforward modeling of abiotic processes.

### **2.1.2. Microbial species and growth**

The model developed here is formulated explicitly for non-growth conditions, assuming that system biomass has reached a quasi-steady-state. This may be inappropriate when representing systems in which biomass growth is significant, e.g., when biomass growth occurs in the field under DOC injection [*North et al.*, 2004; *Chang*, 2005]. However, models that do not consider biomass concentrations can be considered appropriate for the following reasons: (i) it may reasonably be expected that during OC injection, the degrading biomass populations attain a maximum

biomass concentration [Jaffé and Rabitz, 1988]. Once the biomass has reached this maximum concentration the system is inherently at quasi-steady-state (with respect to biomass), and the model is therefore appropriate; (ii) methods of measurement for microbial rates at the field-scale such as push-pull tests [e.g., Schroth *et al.*, 1998; North *et al.*, 2004] generate bulk reaction rates that implicitly take account of biomass. Therefore exclusion of biomass concentration from the model allows a more accurate parameterization of the system microbial rates (assuming the field test is conducted for the same time scale and under similar conditions to the modeling exercise); (iii) the majority of experimental studies investigating U(VI) reduction rates are conducted under non-growth conditions, making it difficult to parameterize accurately for growth conditions; (iv) since the modeling interest here is on global biogeochemical processes rather than microbial populations, explicit representation of biomass is not necessary in systems at quasi-steady state, since microbial populations are in fact dependent variables linked to substrate concentrations [Wang and Papenguth, 2001]. The results of Thullner *et al.* [2005], in which the authors compared different microbial modeling approaches to biodegradation of lactate in a sand column, further support this; and (v) in certain cases non-growth conditions may actually better represent biomineralization at the field-scale due to substrate competition between different bacterial populations [Truex *et al.*, 1997].

The microbial groups responsible for TEA processes are typically classified by the EAs used. The principal TEA processes in the subsurface are aerobic respiration, denitrification, manganese reduction, iron reduction, sulfate reduction and methanogenesis [Stumm and Morgan, 1996].

DMRB capable of U(VI) reduction encompass a range of bacterial species, including *Geobacter* [Lovley *et al.*, 1991; Holmes *et al.*, 2002; Finneran *et al.*, 2002a; Anderson *et al.*, 2003; North *et al.*, 2004; Suzuki *et al.*, 2005], fermentative anaerobic *Clostridium* [Francis *et al.*, 1994], *Shewanella* [Tebo and Obraztsova, 1998; Lovley *et al.*, 1991; Wielinga *et al.*, 2000; Frederickson *et al.*, 2002], *Desulfotomaculum* [Ganesh *et al.*, 1999] and *Desulfovibrio* [Lovley and Philips, 1992b; Sani *et al.*, 2004; Spear *et al.*, 2000; Suzuki *et al.*, 2005]. In addition to U(VI) reduction, DMRB have been shown to be capable of reducing nitrate [Finneran *et al.*, 2002a], Fe(III) [Holmes *et al.*, 2002], Mn(IV) [Tebo and Obraztsova, 1998] and sulfate [Lovley and Philips, 1992; Lovley *et al.*, 1993; Ganesh *et al.*, 1999; Spear *et al.*, 2000; Sani *et al.*, 2004; Suzuki *et al.*, 2005].

Most groundwater sediments are host to a variety of microbial species which are, collectively, capable of carrying out the full range of TEA processes (in DMRB-related studies see, for e.g., Anderson *et al.* [2003], North *et al.* [2004] and Suzuki *et al.* [2005]). The dominant microbial consortium is likely to change as the EAs utilized by each bacterial group are progressively depleted [Anderson *et al.*, 2003]. Each TEA process, or the microbial group(s) responsible for the TEA process(es), is modeled as degrading DOC (first step of each TEA process) at a separate rate. Microbial groups are therefore implicitly considered, since DOC oxidation is explicitly dependent on the EA being consumed. The progress of the second step of each TEA process is then modeled according to chemical (equilibrium) thermodynamics. The injected DOC compound is represented by CH<sub>2</sub>O. DOC degradation via microbially mediated oxidation results in the release of zero-valent carbon into solution. By formulating the DOC fermentation rate as dependent on the concentration of DOC and the relevant

EA, the kinetics of the bacteria are automatically dependent upon the concentrations of both [e.g., *Hunter et al.*, 1998; *Brun and Engesgaard*, 2002]. The DOC degradation rate is defined by the Michaelis-Menten kinetic formulation

$$\frac{\partial C_{\text{DOC}}}{\partial t} = -W(C_{\text{EA}}, \chi_{\text{EA}})\mu_{\text{EA}}\left(\frac{C_{\text{DOC}}}{K_{\text{DOC}} + C_{\text{DOC}}}\right)\left(\frac{C_{\text{EA}}}{K_{\text{EA}} + C_{\text{EA}}}\right), \quad (1)$$

where  $\mu_{\text{EA}}$  is the maximum DOC oxidation rate which is dependent on the EA being consumed ( $\text{T}^{-1}$ );  $C_{\text{EA}}$  is the concentration for the EA being consumed ( $\text{ML}^{-3}$ ),  $K_{\text{DOC}}$  and  $K_{\text{EA}}$  are the half saturation constants for DOC and the EA being consumed, respectively. In a system with several EAs, the degradation rate follows that which is the most energetically favorable. This constraint is modeled in (1) using the inhibition function  $W$  [*Barry et al.*, 2002].  $\chi_{\text{EA}}$  is a minimum concentration of the EA for the respective TEA process to occur, as utilized by *Wang et al.* [2003]. When the value of  $C_{\text{EA}}$  is above the value of  $\chi_{\text{EA}}$ , the function  $W$  takes the value one and the respective TEA process proceeds; whereas when the value of  $C_{\text{EA}}$  is below the value of  $\chi_{\text{EA}}$ , the function  $W$  takes the value zero and the respective TEA process does not proceed. As noted, this approach ensures that the utilization of zero-valent carbon follows the desired order. It further permits DOC oxidation utilizing U(VI) as the EA to occur concurrently with DOC oxidation utilizing Fe(III) or sulfate as the EA as has been documented [*Finneran et al.*, 2002a,b; *Holmes et al.*, 2002; *Senko et al.*, 2002; *Anderson et al.*, 2003; *North et al.*, 2004]. It should be noted that secondary redox reactions and mineral precipitation/dissolution reactions are not modeled as kinetic reactions, but according to chemical equilibrium. The model may not therefore effectively represent systems in which these processes are slow.

The stoichiometry defined in the model, together with the defined reaction network set in the MINTEQA2 4.00 database, states that two moles of U(VI) are reduced and two moles of UO<sub>2</sub> produced for every mole of CH<sub>2</sub>O oxidized [Wang and Papenguth, 2001; Roden and Scheibe, 2005].

### **2.1.3. DMRB & redox sequence**

Generally, DMRB activity tends to conform to typical TEA process sequencing [Abdelouas *et al.*, 1998]. For example, nitrate must be reduced prior to Fe(III) or U(VI) reduction [DiChristina, 1992; Lovley and Chapelle, 1995; Finneran *et al.*, 2002a,b; Senko *et al.*, 2002; Istok *et al.*, 2004]. This may be due to either DMRB preference for nitrate as an EA or the fact that the presence of nitrate would rapidly reoxidize formerly reduced Fe(II) or U(IV) to Fe(III) and U(VI), respectively [Finneran *et al.*, 2002a]. However, extensive and stable U(VI) reduction has also been demonstrated by biostimulation at a field site with high nitrate concentrations in which *Clostridia* and *Clostridia*-like organisms were the dominant bacterial species [Smith *et al.*, 2006]. Furthermore, the Fe(III)-, U(VI)- and nitrate-reducing *Geobacter metallireducens* has been found to reduce Fe(III) and U(VI) in the presence of nitrate when it had been grown with Fe(III) as the EA, but not when it had been grown with nitrate [Finneran *et al.*, 2002a]. It is therefore likely that the sequence of TEA processes is sensitive to both bacterial species and the history of the geochemical environment.

Following nitrate reduction, U(VI) and Fe(III) reduction typically occur concurrently [Finneran *et al.*, 2002a,b; Holmes *et al.*, 2002; Anderson *et al.*, 2003; North *et al.*, 2004] and prior to sulfate reduction [Finneran *et al.*, 2002a,b]. It is

known that numerous sulfate reducers can reduce U [Tebo and Obratzsova, 1998; Lovley and Philips, 1992; Lovley et al., 1993; Ganesh et al., 1999; Spear et al., 2000; Sani et al., 2004; Suzuki et al., 2005]. Ortiz-Bernard et al. [2004] biostimulated Rifle, Colorado (USA) sediments with acetate and found U(VI) reduction halted when Fe(III) was depleted and sulfate reduction became the dominant process. However, Spear et al. [2000] reported concurrent U(VI) and sulfate reduction by *Desulfovibrio desulfuricans*, with an increase in U(VI) reduction rate in the presence of sulfate. The biostimulation project by Anderson et al. [2003] at the U(VI)-contaminated Rifle field site found an increase in U(VI) when the dominant TEA processes switched from Fe(III) to sulfate reduction. Senko et al. [2002] observed concomitant U(VI) and sulfate reduction in sediment incubations in which sulfate did not inhibit U(VI) reduction, however slight inhibition of U(VI) reduction by sulfate was witnessed in associated push-pull tests. Holmes et al. [2002], however, deduced that sulfate-reducing microorganisms were not important for the biostimulated U(VI) reduction in Shiprock, New Mexico (USA) sediments, and Lovley and Philips [1992a] noted that the presence of sulfate had no impact on U(VI) reduction by the sulfate-reducing bacterium *Desulfovibrio desulfuricans*.

It appears that the specific sequence of TEA processes depend on the geochemical environment, the biogeochemical history, and the DMRB strain(s) present, some of which may be capable of sulfate or metal reduction without being capable of U(VI) reduction. The dependence of U(VI) reduction rates on DMRB strain, EA, and EDs further support this [Liu et al., 2002]. The details of these complex relationships are not yet well understood. Therefore, the sequence of TEA processes in the model



developed here is controlled by accepted thermodynamic equilibrium. Specifically, the network of equations in the MINTEQA2 4.00 database is employed.

#### **2.1.4. Porous media clogging**

Porous media may be subject to clogging via the excessive accumulation of minerals or biomass [VanGulcka and Rowe, 2004]. Media clogging may obstruct the flow channels between the mobile and immobile regions, subsequently decreasing the mass transfer rate between regions and affecting U(VI) immobilization. The present model, however, is developed for systems in which the impacts of media clogging are negligible. For example, *Abdelouas et al.* [1998a] stimulated DMRB at a uranium mill tailings site near Tuba City, Arizona (USA) and found no evidence of pore clogging due to either biomass accumulation or mineral formation. The hydrological properties of the sandstone media investigated were not changed by increased bacterial activity. In addition, it is noted that at the maximum mineral concentrations encountered in the simulations conducted in this work, the sum of all mineral volumes accounts for just 0.2% of aquifer pore space. This is considered negligible with regard to aquifer flow plugging. Systems that experience significant plugging due to low quantities of mineral precipitation or biomass growth may display different behavior to that presented in this work. It is acknowledged that bioclogging can be significant in the vicinity of injection/withdrawal wells (e.g., for EDs). However, the quasi-steady-state biomass assumption employed implies that the model is most applicable to the treatment (i.e., bioimmobilization) zone located between wells where this effect is assumed to be minimal.

## **2.2 Dual porosity media and transport equations**

It is generally accepted that the traditional Fickian advection-dispersion model does not capture the solute transport behavior exhibited in multi-porosity heterogeneous porous media adequately, particularly at the field scale. This is because fractures and other high-hydraulic conductivity (K) flow paths in heterogeneous porous media provide rapid transfer of contaminants into aquifers, while low-K zones act as diffusion-limited reservoirs for contaminants and other aqueous species. Such preferential flow paths have been exposed, for example, through use of dye tracers [Jørgensen *et al.*, 2004]. Groundwater flow systems showing this dual-domain flow phenomenon have been documented in the literature both in column flow experiments [Grisak *et al.*, 1980; Haws *et al.*, 2004, 2005] and at the field scale [Sidle *et al.*, 1998; Ryan *et al.*, 2000; Julian *et al.*, 2001].

Groundwater flow models for heterogeneous porous media that display this dual-domain transport behavior have been characterized by two separate flow zone continua. These two zones conceptually combine the effects of local flow variation and inter-region diffusion [Li *et al.*, 1994], such that existing concentration gradients are adequately captured. The first zone, traditionally conceptualized as the “mobile” region, exhibits mass transfer dominated by advective (or relatively high-velocity) flows. The second zone, traditionally conceptualized as the “immobile” region, exhibits mass transfer dominated by diffusive mass flux. The immobile region therefore effectively acts as a temporary diffusion-limited sink, capable of sequestering U(VI) or other chemical species. Modeling systems with heterogeneous hydraulic conductivity employing dual-domain mass transfer approaches has more successfully reproduced observed solute transport behavior than single domain formulations [Bajracharya and Barry, 1997; Feehley *et al.*, 2000].

Advective-diffusive transport occurs within the mobile region only. The partial differential equation describing saturated one-dimensional chemical transport under transient fluid flow conditions in the mobile region is [van Genuchten and Wierenga, 1976]

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_i \frac{\partial C_i}{\partial t} = -\theta_m v_m \frac{\partial C_m}{\partial x} + \theta_m (D_e + a v_m) \frac{\partial^2 C_m}{\partial x^2} - \theta_m \frac{\partial q_m}{\partial t} - \theta_i \frac{\partial q_i}{\partial t}, \quad (2)$$

where subscript  $m$  indicates mobile and  $i$  indicates immobile,  $C$  is the concentration of a chemical species in solution ( $\text{ML}^{-3}$ ),  $v_m$  is the average pore-water velocity in the mobile region ( $\text{LT}^{-1}$ ),  $q$  is a source/sink term which accounts for geochemical changes due to both kinetic and equilibrium reactions ( $\text{ML}^{-3}\text{T}^{-1}$ ),  $x$  is the distance along the spatial domain (L),  $t$  is time (T), and  $\theta_m$  and  $\theta_i$  are the media porosities in the mobile and immobile regions ( $\text{L}^3\text{L}^{-3}$ ), respectively.  $D_e$  is the effective diffusion coefficient ( $\text{L}^2\text{T}^{-1}$ ) and  $a$  is the dispersivity (L). The total porosity of the media is the sum of the mobile and immobile region porosities

$$\theta_T = \theta_m + \theta_i. \quad (3)$$

In the present work, DP functionality is utilized such that high permeability porous media regions in the aquifer are represented by mobile zones, whilst regions of relatively slow flow are represented by immobile regions. Mass exchange between mobile and immobile groundwater occurs via a first-order mixing process, which is typically assumed to be driven by a concentration gradient and characterized by a mass transfer rate [e.g., *Grisak and Pickens*, 1980; *Tang et al.*, 1981; *Simunek et al.*,

2003; *Haws et al.*, 2004; *Gwo et al.*, 2005]. In the PHREEQC model, an immobile cell is associated with each mobile cell. The mass transfer exchange between the mobile and immobile cells is given by *van Genuchten and Wierenga* [1976]

$$\theta_i \frac{\partial C_i}{\partial t} \left( 1 + \frac{\partial q_i}{\partial C_i} \right) = \gamma (C_m - C_i), \quad (4)$$

where  $C$  is a geochemical species,  $q_i$  is a source/sink term for the immobile region which accounts for geochemical changes due to both kinetic and equilibrium reactions, and  $\gamma$  is the first order mass transfer rate ( $T^{-1}$ ).

### **2.3 Surface complexation**

Natural systems may exhibit complex sorption behavior. Specifically, U(VI) adsorption is significantly influenced by pH and carbonate concentration, as well as changes in aqueous speciation [*Dzombak and Morel*, 1990; *Waite et al.*, 1994]. However, numerous reactive transport models ignore this, instead adopting a constant- $K_d$  modeling approach for U(VI) sorption [e.g., *Wang and Papenguth*, 2001; *Wang et al.*, 2003; *Roden and Scheibe*, 2005]. Surface complexation models (SCM) account for pH changes, the effect of variations in solution chemistry, and the complexing properties of sorbing surface sites [*Langmuir*, 1997]. SCM models assume adsorption occurs on specific surface sites, allowing for a number of specific sites to be utilized by the sorbent.

*Waite et al.* [1994] developed a model that built on the diffuse double layer (DDL) model [*Stumm et al.*, 1970; *Huang and Stumm*, 1973; *Dzombak and Morel*, 1990].

*Barnett et al.* [2000] hypothesized that iron oxides control U(VI) sorption. *Barnett et al.* [2002] further developed the model by *Waite et al.* [1994] to simulate the U(VI) sorption behavior of three heterogeneous subsurface media (from the US Department of Energy Oak Ridge, Savannah River, and Hanford Reservation sites). The *Barnett et al.* [2002] model successfully predicted the pH-dependent adsorption of the three different media, with only slight differences between observations and predictions in the location of adsorption isotherm pH edges and the maximum amount of U(VI) adsorbed. While the model has been observed to overestimate retardation in the pH region of maximum adsorption on the adsorption isotherm, it remains one of the most accurate models in the literature for U(VI)-iron oxide sorption.

It should be noted that the *Barnett et al.* [2002] model uses molality as the activity of surface species, whereas the present model uses mole fraction. This difference gives equivalent answers for monodentate surfaces, but not for the bidentate surfaces as modeled in the present work. Furthermore, the *Barnett et al.* [2002] model uses a different equation for mole balance and mass action: the mass balance equation is defined such that bidentate surfaces are formed with two  $\equiv\text{FeOH}$  groups for every mole of U(VI) absorbed, but the mass action equations are defined such that the first power of the  $\equiv\text{FeOH}$  concentration is used rather than the second power. The SCM used in the present model instead uses balanced equations; the second power of the  $\equiv\text{FeOH}$  concentration is used in the mass action equations.

The SCM adopted in this work includes the chemical reactions and equilibrium constants from *Barnett et al.* [2002], presented in Table 1. The surface complexation model parameters (number of reactive sites, equilibrium constants, site densities, and

specific surface areas) of *Barnett et al.* [2002] are adopted in this work. In addition to these reactions, the aqueous-phase reactions provided by the MINTEQA2 4.00 database [*Allison et al.*, 1991] are included. Due to these additions, the current SCM model predicts slightly different behavior from that presented in *Barnett et al.* [2002]. Figure 1 provides the pH isotherm output for this formulation of the model, as well as the U(VI) sorption behavior of the three heterogeneous subsurface media originally published by *Barnett et al.* [2002]. The model accurately predicts the experimental data providing confidence in its suitability for this work.

This surface complexation model is employed in all subsequent transport simulations reported in this work, and surface complexation is assumed to act throughout the domain. Ferrihydrite is considered the only iron oxide present, as was assumed in the surface complexation models developed by *Barnett et al.* [2002] and *Waite et al.* [1994]. Complexed U(VI) is unavailable to bacteria for biologically induced reduction [*Ortiz-Bernard et al.*, 2004; *Jeon et al.*, 2004].

U(VI)-clay sorption processes may be included within the present model code. However, the present model has been developed for systems in which U(VI) sorption is dominated by U(VI)-iron oxide surface complexation. Systems in which U(VI)-clay sorption is significant are likely to exhibit different behavior, and may display decreased U(VI) desorption during Fe(III) reduction [*Liu et al.*, 2005]. Likewise, the model does not consider DOC-complexed U and is therefore relevant to systems in which either DOC-complexed U concentrations are insignificantly low or in which DOC-complexed U is insignificant in facilitating U transport. *Ranville et al.* [2006], for example, found that less than 3% of U in an aquifer was complexed to DOC. It is

acknowledged that that U(VI) binding with certain types of organic matter (e.g., humic acid) may be significant and the model may be inappropriate for such systems.

### 3 Comparison with existing model

The developed model was compared to that of *Wang et al.* [2003], in order to (i) build confidence in the model's ability to capture the relevant behavior and, (ii) compare results with a simulator that employs different model formulations (for secondary redox reactions, mineral precipitation/dissolution and surface complexation). This approach was adopted in the absence of appropriate laboratory data. The model of *Wang et al.* [2003] is a one-dimensional finite-difference reactive transport model developed to simulate biogeochemical processes during U(VI) contaminated aquifer bioremediation. *Wang et al.* [2003] present a simulation of oxic recharge water rich in DOC entering a uranium-contaminated aquifer. The aquifer contains EAs typical of uranium-contaminated environments. The simulated geochemical conditions, including the concentrations of the EAs, are detailed in Table 2.

The present model was operated in SP mode and was parameterized so as to reproduce the *Wang et al.* [2003] scenario as closely as possible. The transport conditions simulated are detailed in Table 3, and the parameters relating to the microbial formulation (equation 1) are listed in Table 4. All parameter values were taken from *Wang et al.* [2003] except the immobile region porosity (DP case) and the mobile-immobile mass transfer, whose values were taken from the literature. Note that the domain is discretized to a finer grid in this work ( $\Delta x = 0.25$  m) than that used by *Wang et al.* ( $\Delta x = 0.5$  m) in order to minimize numerical artifacts.

Every effort was made to use the same conditions reported in *Wang et al.* [2003]. However, the differences in modeling approach between the two models mean the



following differences remain: (i) the U(VI) adsorption model, in which *Wang et al.* [2003] use an empirical isotherm adsorption model whereas this work uses a SCM (see Section 2.3), and (ii) the approach to secondary redox reactions, which are modeled kinetically by *Wang et al.* [2003] whereas the PEA is adopted here (see Section 2.1.1). The implications of these differences are discussed below.

A Dirichlet boundary condition is used at the upstream end of the domain and the domain is considered to be physically semi-infinite (actual simulated domain was 50 m). *Wang et al.* [2003] do not explicitly state which minerals are present in their simulations. In this work, Fe(III) and Mn(IV) are present in the form of ferrihydrite and pyrolusite, as these minerals are likely to be present in typical aquifers. Uraninite is not initially present but is capable of forming. Carbonate, while often found in natural groundwaters, is omitted from the initial aquifer and recharge water here to provide similarity with *Wang et al.* [2003]. Note, however, that its presence increases due to microbial activity during biostimulation. It is acknowledged that the inclusion of carbonate may significantly alter the results, and thus it may not be possible to extrapolate the results presented here to such scenarios. All parameters were obtained independently and the comparison between the two models was made without calibration of parameter values.

Figures 2-7 show the simulated spatial concentration distributions of various species and minerals in the domain after one year of biostimulation. The results of *Wang et al.* [2003] are also detailed in these figures: if a figure does not include *Wang et al.* [2003] data, this is because such data was not provided.

Figure 2 presents the DOC, pH and carbonate concentration along the flow path. Figure 3 presents the spatial distribution of EAs compared with those reported by *Wang et al.* [2003], demonstrating that the model captures the characteristic geochemical behavior reported in their work. The domain is free to experience biologically induced reduction anywhere along its length. Under the conditions of this system, the spatial region of the domain experiencing reduction is  $x = 4$  to 12 m. Figure 2 reveals that the DOC entering the domain is quickly oxidized, and the changes in pH and carbonate qualitatively reflect those which occur in biostimulated systems [e.g., *Wan et al.*, 2005; *Luo et al.*, 2007]. Note, however, that typical porous media may exhibit a smaller pH change than predicted, since a higher buffering capacity is possible than accounted for in this comparison scenario [cf. *Abdelouas et al.*, 2000; *Anderson et al.*, 2003].

Figure 3 reveals that, as expected, the EAs are reduced sequentially in order of the most energetically favorable and a region forms in the domain which favors reduction ( $4 \text{ m} < x < 12 \text{ m}$ ). Figure 2 shows that carbonate concentration and pH increase just downgradient of the reductive region. In addition, Figure 4 illustrates that Fe and Mn oxyhydroxides are progressively reduced and dissolved whilst reduced species such as Fe(II), Mn(II) and  $\text{HS}^-$  accumulate also just downgradient of the reductive region. These geochemical changes are characteristic of U(VI) immobilization in biostimulated sites and sediments [e.g., *Abdelouas et al.*, 1998; *Finneran et al.*, 2002b; *Holmes et al.*, 2002], providing confidence in both models.

The abiotic reactions in the present model proceed similarly to those reported by *Wang et al.* [2003]: Fe(III) and Mn(IV) reduction appears to be less favorable than

nitrate (Figure 3), but this is due to the occurrence of simultaneous abiotic reactions. The high  $\text{HS}^-$  concentration in the reduced region may reduce Fe(III) and Mn(IV) abiotically before bacterial reduction is possible. These processes appear to be enhanced in the present model, resulting in the reduced species Fe(II) and  $\text{HS}^-$  exhibiting lower concentrations compared to those predicted by *Wang et al.* [2003] (Figure 4). This difference is likely due to the different formulations for secondary redox reactions. While it is difficult to find comprehensive experimental data in which all relevant parameters have been measured, confidence in the model(s) is provided by the qualitative match achieved between the results presented here and the behavior of similar systems reported in the literature [e.g., *Abdelouas et al.*, 1998; *Finneran et al.*, 2002b; *Holmes et al.*, 2002; *Ortiz-Bernard et al.*, 2004].

Figure 5 reveals that the total dissolved U(VI) is reduced in the reductive region of the domain once it is energetically favored as an EA. The spatial position of the U(VI) concentration decrease and increase is somewhat different for the two model outputs, reflecting the differing reductive region in the domain noted previously (Figure 3). *Wang et al.* [2003] do not specify if uraninite may form in their model, whereas the present model allows its formation in order to account for known DMRB activity in biostimulated subsurface environments. Due to this likely difference in approach, the observed U(IV) in solution may not be comparable between the two models. Note that the U(IV) concentration for the present model is so low as to not be visible in Figure 5. Figure 6 presents the U(IV) (as in Figure 5) and uraninite concentrations for the model developed in this work. The uraninite is predicted to reside in the reductive region of the domain, with a low U(IV) concentration present at the downgradient end of this region where the domain becomes more oxidizing.

Significantly, in Figure 5 the U(VI) concentration for the present model output is observed to spike downgradient (peaking at  $x = 14$  m) of the reductive region, and the maximum concentration of this spike increases as time progresses (data not shown). This phenomenon was not observed in the *Wang et al.* [2003] model output. This behavior is a consequence of the more complex surface complexation model used in this work, and it occurs for multiple reasons. First, the pH in the downgradient U(VI)-spike region has increased due to biological activity (Figure 2,  $12 \text{ m} < x < 18 \text{ m}$ ) resulting in a less favorable condition for adsorption (see Figure 1). Second, a snow-plow [*Starr and Parlange, 1979; Barry et al., 1983*] effect occurs: as the ferrihydrite in the reductive region is reduced, the U(VI) previously complexed to its surface desorbs, causing a net increase in U(VI) in solution downstream of the reductive region. Third, the high carbonate concentrations in this region (Figure 2) may cause increased desorption (Figure 1). All these factors may increase the propensity for U(VI) to desorb. Figure 7 demonstrates that the concentration of all U-sorbed species (i.e.,  $\equiv\text{Fe}_s\text{O})_2\text{UO}_2 + (\equiv\text{Fe}_w\text{O})_2\text{UO}_2 + (\equiv\text{Fe}_s\text{O})_2\text{UO}_2\text{CO}_3^{2-} + (\equiv\text{Fe}_w\text{O})_2\text{UO}_2\text{CO}_3^{2-}$ ) reduces in regions where ferrihydrite is less abundant ( $4 \text{ m} < x < 12 \text{ m}$ ). The more ferrihydrite that is reduced, the more desorption occurs and the greater the concentration of the U(VI) spike. Where the ferrihydrite concentration and pH decrease to initial levels (at  $x > 18 \text{ m}$ ), the U(VI) concentration also decreases (Figure 5).

It should be noted that systems exhibiting significant U(VI)-clay sorption may not display the desorption-induced U(VI) concentration spike since, upon iron oxide reduction, U(VI) previously sorbed to iron-oxide may consequently sorb to clay

minerals with the result that net aqueous U(VI) concentrations do not change significantly. *Liu et al.* [2005] reported such a phenomenon. However, this observation was based on data where only ~50% of the Fe(III) oxide fraction was biologically reduced. Systems experiencing a greater degree of Fe(III) oxide reduction, like the system explored in the present work, may experience marked changes in U(VI) sorption behavior if insufficient clay sorption sites are available to complex with the Fe(III)-desorbed U.

## 4 Impact of dual porosity media

Simulations were conducted in order to investigate the potential impact of DP media on the effectiveness of uranium immobilization. The SP case presented in Section 3, involving homogeneous sand, is compared here to a similar scenario characterized by a combined low-K and high-K porous medium (e.g., interspersed sand and clay stringers).

Microbial activity is considered here to take place in both the mobile and immobile regions, such that the bacteria are present throughout the total porosity of the media for both the SP and DP cases. The initial geochemical conditions are maintained the same for all SP and DP simulations (as defined in Table 2, initial conditions). This is because differing geochemical conditions of the immobile region may impact the comparison, since the presence of EAs more thermodynamically favorable than uranium in this region will cause a net delay in bioimmobilization. The initial geochemical conditions are therefore maintained the same for all SP and DP simulations (as defined in Table 2, initial conditions), as are the transport conditions (Table 3) and the microbial parameter values (Table 4).

As the ultimate aim of this bioremediation strategy is significant immobilization of U(VI), the metric used to compare results is the concentration of U(VI) passing a specific distance (10 m) downgradient of the DOC injection point. Figure 8 presents the results of simulations for SP and DP systems with  $\theta_m = 0.1$  and  $\theta_s = 0.25$ . Results are shown for (i) simulations in which the presence of carbonate has been omitted from the aquifer influent and the initial aquifer groundwater, in order to provide similarity with *Wang et al.* [2003] and (ii) simulations in which carbonate is included

(1 mmol l<sup>-1</sup> for  $x > 0$ ,  $t = 0$  and for  $x = 0$ ,  $t$ ) in the aquifer influent and the initial aquifer groundwater. In the DP system, U(VI) immobilization is significantly delayed relative to the SP system. This is because (i) U(VI) remains sequestered in the immobile region and diffusion limits the rate of its release to the mobile region, and (ii) the bacteria first reduce the other EAs diffusing out of the immobile region before U(VI) becomes energetically preferable for them. In both SP and DP systems, the U(VI) concentration is observed to increase before immobilization takes place when carbonate is not present. When carbonate is present, the maximum concentration of the U(VI) spike before immobilization is predicted to be reduced. This occurs because U(VI) adsorption increases due to both a pH decrease induced by the presence of carbonate and an increase in the carbonate sorption species, and supports existing experimental evidence which suggests that reduced carbonate or carbonate mineral presence results in significant increases in U(VI) adsorption [Dong *et al.*, 2005]. Note, however, that the time to U(VI) immobilization remains the same. This suggests that the presence of carbonate may reduce the short-term elevated U(VI) concentrations exiting the biostimulated zone, yet it appears not to impact the overall efficiency of remediation significantly.

## **5 Impact of microbial residence and porosity**

Simulations were conducted for three different microbial residency conditions: bioactivity present in the immobile region, the mobile region, and both regions. The simulations consider the same conditions as the DP simulations in Section 4. These simulations use the same transport conditions (Table 3) and the microbial parameter values (Table 4). However, the geochemical boundary conditions have been modified from those used by Wang *et al.* [2003]. The new conditions are presented in Table 5

and are deemed more appropriate to real sites than those used by *Wang et al.* [2003] because (i) the influent U(VI) concentration is above the US Federal Register limit [*Federal Register*, 1995] rather than below it, (ii) calcium is present, and (iii) the geochemical parameters used are based on reported mean field site values (for the Area 2 uranium-contaminated field site at the Oak Ridge Field Research Center, <http://www.esd.ornl.gov/nabirfrc/>) so as to be representative of uranium-contaminated aquifers. The time at which the U(VI) concentration falls below the existing groundwater protection standard of 0.18  $\mu\text{M}$  [*Federal Register*, 1995] in the mobile region at 10 m downstream of the DOC injection point is used as the metric for the comparison of different simulation scenarios (this is, for example,  $t = 0.875$  y for the SP system plotted in Figure 8). In order to compare immobilization efficiency in different porous media types, the ratio of mobile to total porosities is used:

$$\beta = \frac{\theta_m}{\theta_m + \theta_i} \quad (5)$$

This ratio tends to be constant for a given medium [*Li et al.*, 1994].

Figure 9 presents the time at which U(VI) falls below the metric level against the porosity ratio  $\beta$  for both a mean and a low mass transfer rate (Table 3) between the mobile and immobile regions. The curves for bioactivity in the mobile and immobile region do not show values below  $\beta = 0.25$  or above  $\beta = 0.64$  due to the long computational times required. Nevertheless it may be safely assumed that the same curve trends continue at  $\beta$  values beyond those shown in Figure 9. When bioactivity occurs in both the mobile and immobile regions the net microbial efficiency is high, resulting in rapid consumption of EAs and faster U(VI) immobilization relative to



either mobile- or immobile-region isolated bioactivity. Further, the time taken to immobilize the U(VI) is independent of the porosity ratio  $\beta$ .

However, when bioactivity occurs in either the immobile or mobile region only, the net microbial efficiency is slower and is demonstrated to vary with  $\beta$ . In the case of immobile-resident bioactivity, mass transfer limitations between the mobile and immobile region limit the bacteria's access to DOC, thereby reducing the net microbial efficiency. As a result, U(VI) immobilization is considerably slower compared to systems in which bioactivity occurs in both regions. As the immobile region porosity becomes smaller relative to the mobile region porosity (increasing  $\beta$ ), the reduced relative porosity of the immobile region yields a reduced pore water volume in which microbial activity takes place, thus reducing the net U(VI) immobilization efficiency. In the case of mobile-resident bioactivity, the reverse situation occurs as  $\beta$  increases: microbially accessible pore water volume increases and the time taken to diminish U(VI) decreases.

Therefore, systems with  $\theta_m < \theta_i$  and microbial activity occurring predominantly in porous media regions of more mobile (higher velocity) pore water will tend to exhibit slower U(VI) immobilization than those with microbial activity occurring predominantly in immobile (low velocity) pore water regions, for systems of comparable biological, geochemical, and transport conditions. In systems in which  $\theta_m > \theta_i$ , this phenomenon reverses: when predominant microbial activity occurs in the mobile region, U(VI) immobilization is more efficient than when microbial activity occurs predominantly in the immobile region. Overall, this agrees with expectations: bioimmobilization is most efficient when biological activity occurs in the highest

porosity region. It should be noted that microbial activity in both regions results in greater remediation efficiency than either of these scenarios. This suggests that, under equivalent bacterial, geochemical (including injected DOC concentration) and transport conditions, variation in porosity ratio does not affect immobilization rate when both regions are bioactive.

## 6 Impact of mass transfer rate

Figure 9 also displays simulations that were conducted to examine the influence of mass transfer rate between the mobile and immobile regions on immobilization efficiency. The base case scenarios presented using the mean mass transfer rate ( $\alpha = 278 \text{ y}^{-1}$ ) were repeated for the high rate ( $\alpha = 1900 \text{ y}^{-1}$ ) and low rate ( $\alpha = 1.6 \text{ y}^{-1}$ , not shown in figure) obtained from real site data (Table 3) across the range of porosity ratios. Note that the results for the high mass transfer rate ( $\alpha = 1900 \text{ y}^{-1}$ ) are very similar to the mean mass transfer rate, indicating a lack of sensitivity to this parameter in this range, and are therefore not shown in Figure 9. The model suggests that U(VI) immobilization efficiency is insensitive to mass transfer rate when bioactivity is limited to the mobile region, regardless of porosity ratio. However, when bioactivity is limited to the immobile region, reduced mass transfer rate causes reduced immobilization efficiency. This occurs because of the reduced rate at which DOC may diffuse to the microbial population. This sensitivity to mass transfer rate increases with increasing porosity ratio (i.e., increasing  $\theta_m$ ) due to the reduced amount of microbial mass available for bioimmobilization.

When the mobile and immobile regions are both bioactive, the immobilization efficiency is not sensitive to mass transfer rate (results shown for low and mean  $\alpha$

values in Figure 9, but not shown for high  $\alpha$  values which are nearly identical to those for mean  $\alpha$  value).

## 7 Conclusions

A biogeochemical reactive transport model was developed for uranium immobilization in both single and dual porosity media. A one-dimensional simulation in a single porosity domain compared well to the *Wang et al.* [2003] model without any model calibration. The geochemical changes predicted are qualitatively characteristic of U(VI) immobilization in biostimulated sites and sediments. More comprehensive experimental data sets are required to conduct the important step of model validation in this field.

The present model predicts a transient increase (“spike”) in U(VI) concentrations downgradient of the treatment zone in systems with insignificant carbonate content. This is due to geochemical changes (carbonate and ferrihydrite concentrations and pH) induced by DMRB which cause desorption of ferrihydrite-complexed U(VI). The increase in downgradient U(VI) appears to be temporary, as desorbed U(VI) is subsequently bioimmobilized as U(IV). It is acknowledged that this phenomenon may be absent in systems in which U(VI) sorption to clay is significant.

U(VI) immobilization is predicted to be significantly delayed in media exhibiting dual porosity behavior relative to more homogeneous systems due to diffusion limitations on all EAs. Simulations indicate that when bioactivity is dominant in only one region, U(VI) immobilization efficiency is dependent on the ratio of the mobile region porosity to the total porosity. This dependence is not observed when both regions are bioactive. Further, the mass transfer rate between the mobile and immobile regions may significantly impact U(VI) immobilization efficiency when

only the immobile region is bioactive, but is less likely to do so when the mobile region or both regions are bioactive.

Multi-region models that assume microbial residence in both “mobile” and “immobile” conceptualized regions may significantly overestimate microbial efficiency and thereby exaggerate predicted remediation effectiveness if biomass is restricted to specific media regions. This highlights the importance of characterizing the bioresidency status of field sites if biogeochemical models are to accurately predict remediation schemes in physically heterogeneous media. Further, bioaugmentation may present a viable option for improving bioimmobilization efficiency in such sites. As yet, no radionuclide-contaminated sites have been proposed for bioaugmentation [*Hazen and Tabak, 2005*] and further research is needed to determine the capabilities and limitations of the technique. Additionally, reoxidation of immobilized uranium should be considered in future work in order to assess the long-term success of bioimmobilization strategies [*Suzuki and Suko, 2006*].

This work assumes that system biomass has reached a quasi-steady-state and therefore does not grow, and that ferrihydrite is the only surface with which U(VI) complexes. While the simulations included the presence of calcium, the effects of high concentrations of calcium or magnesium are not considered. These may impact U(VI) sorption [*Dong et al., 2005*] and U(VI) reduction [*Brooks et al., 2003*]. Despite these simplifications, it is expected that the results are broadly representative. It should be noted that the model assumed instantaneous and complete mixing within the immobile region (equation (4)). The results presented here may therefore overestimate immobilization rates in systems in which mass transfer is controlled via

diffusion within the immobile region, rather than at the boundary between mobile and immobile regions. For the one-dimensional model presented, it is expected that this assumption is reasonable for thin clay stringers surrounded by an active flow zone. When the scenario differs from this (e.g., an open fracture within a substantial clay matrix) it might be expected that observations in the mobile region downgradient of the treatment zone would be influenced more slowly by the immobile region than predicted by the model. It should additionally be noted that predictions regarding the influence of immobile regions (or regions where the dominant solute movement is controlled by diffusion) are known to be sensitive to system boundary and initial conditions [Haws *et al.*, 2007], further emphasizing that the presented model and results are most relevant for systems closely approximated by the scenarios described.

## 8 Notation

$a$	dispersivity, L
$C$	concentration, subscripts $m$ and $i$ indicate the mobile and immobile region, respectively; other subscripts indicate the chemical species, $\text{ML}^{-3}$
$D_e$	effective diffusion coefficient, $\text{L}^2\text{T}^{-1}$
$K$	half saturation constant; subscripts indicate the chemical species, $\text{ML}^{-3}$
$q$	source/sink term for chemical reactions, $\text{ML}^{-3}$
$t$	time, T
$v_m$	pore water velocity, $\text{LT}^{-1}$
$x$	distance, L
$W$	step function
$\beta$	porosity ratio $\theta_m/(\theta_m + \theta_i)$
$\gamma$	mobile-immobile mass transfer coefficient, $\text{T}^{-1}$
$\theta_m$	mobile region porosity, $\text{L}^3\text{L}^{-3}$
$\theta_i$	immobile region porosity, $\text{L}^3\text{L}^{-3}$
$\theta_T$	total media porosity (equal to $\theta_m + \theta_i$ ), $\text{L}^3\text{L}^{-3}$
$\mu_{EA}$	maximum DOC fermentation (subscripted) electron acceptor, $\text{ML}^{-3}\text{T}^{-1}$
$\chi_{EA}$	limiting concentration of (subscripted) electron acceptor for TEA process switching, $\text{ML}^{-3}$

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## 11 Figure Captions

Figure 1. Surface complexation model validation.

Figure 2. Model comparison: DOC, carbonate and pH spatial profiles of the present model after one year of biostimulation. *Wang et al. (2003)* data not available.

Figure 3. Model comparison: Electron acceptor species after one year of biostimulation. Dashed lines are the present model, solid lines are *Wang et al. (2003)* model.

Figure 4. Model comparison: Reduced geochemical species after one year of biostimulation. Dashed lines are present model, solid lines are *Wang et al. (2003)* model.

Figure 5. Model comparison: total U(IV) (thin lines) and total U(VI) (thick lines) after one year of biostimulation. Dashed lines are present model, solid lines are *Wang et al. (2003)* model.

Figure 6. Model comparison: Present model output for uranium species after one year of biostimulation. *Wang et al. (2003)* output unknown for uraninite.

Figure 7. Spatial profile of sorbed species and ferrihydrite after one year of biostimulation for the present model.

Figure 8. Total U(VI) concentration passing  $x = 10$  m in single porosity (SP) and dual porosity (DP) mobile region for simulation both with and without carbonate.  $\theta_m = 0.1$ ,  $\theta_i = 0.25$ .

Figure 9. Time at which total U(VI) is immobilized for bioactivity in different regions at various porosity ratios, for both low and mean value mobile-immobile mass transfer rate.

**Table 1.** Surface Complexation Model Reactions and Parameters.

<b>U(VI) aqueous complexation reactions</b>		<b>Log K</b>
$\text{UO}_2^{2+} + \text{H}_2\text{O} \rightarrow \text{UO}_2\text{OH}^+ + \text{H}^+$		-5.41
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2 + 2\text{H}^+$		-12.23
$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$		-20.00
$\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+$		-32.57
$2\text{UO}_2^{2+} + \text{H}_2\text{O} \rightarrow (\text{UO}_2)_2(\text{OH})^{3+} + \text{H}^+$		-2.44
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightarrow (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$		-5.79
$3\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightarrow (\text{UO}_2)_3(\text{OH})_4^{2+} + 4\text{H}^+$		-12.25
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \rightarrow (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$		-16.22
$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightarrow (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$		-31.29
$4\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightarrow (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$		-22.62
$\text{UO}_2^{+2} + \text{H}_2\text{CO}_3 \rightarrow \text{UO}_2\text{CO}_3 + 2\text{H}^+$		-6.80
$\text{UO}_2^{+2} + 2\text{H}_2\text{CO}_3 \rightarrow \text{UO}_2(\text{CO}_3)_2^{2-} + 4\text{H}^+$		-15.90
$\text{UO}_2^{+2} + 3\text{H}_2\text{CO}_3 \rightarrow \text{UO}_2(\text{CO}_3)_3^{4-} + 6\text{H}^+$		-26.45
$2\text{UO}_2^{+2} + 3\text{H}_2\text{O} + \text{H}_2\text{CO}_3 \rightarrow (\text{UO}_2)_2\text{CO}_3(\text{OH})^{3-} + 5\text{H}^+$		-18.07
<b>Surface complexation reactions<sup>a</sup></b>		<b>Log K</b>
$2\equiv\text{Fe}_s\text{OH} + \text{UO}_2^{2+} \rightarrow (\equiv\text{Fe}_s\text{O})_2\text{UO}_2 + 2\text{H}^+$		-2.57
$2\equiv\text{Fe}_w\text{OH} + \text{UO}_2^{2+} \rightarrow (\equiv\text{Fe}_w\text{O})_2\text{UO}_2 + 2\text{H}^+$		-6.28
$2\equiv\text{Fe}_w\text{OH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 \rightarrow (\equiv\text{Fe}_w\text{O})_2\text{UO}_2\text{CO}_3^{2-} + 4\text{H}^+$		-16.43
$2\equiv\text{Fe}_s\text{OH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 \rightarrow (\equiv\text{Fe}_s\text{O})_2\text{UO}_2\text{CO}_3^{2-} + 4\text{H}^+$		-12.34
$\equiv\text{Fe}_{s,w}\text{OH} + \text{H}^+ \rightarrow \equiv\text{Fe}_{s,w}\text{OH}_2^+$		6.51
$\equiv\text{Fe}_{s,w}\text{OH} \rightarrow \equiv\text{Fe}_{s,w}\text{O}^- + \text{H}^+$		-9.13
$\equiv\text{Fe}_{s,w}\text{OH} + \text{H}_2\text{CO}_3 \rightarrow \equiv\text{Fe}_{s,w}\text{CO}_3\text{H} + \text{H}_2\text{O}$		2.90
$\equiv\text{Fe}_w\text{OH} + \text{H}_2\text{CO}_3 \rightarrow \equiv\text{Fe}_w\text{CO}_3^- + \text{H}_2\text{O} + \text{H}^+$		-5.09
<b>Model parameters</b>		<b>Value</b>
Strong surface sites (sites per mole ferrihydrite)		0.004
Weak surface sites (sites per mole ferrihydrite)		0.2
Surface area of ferrihydrite ( $\text{m}^2 \text{mole}^{-1}$ )		33600

<sup>a</sup>Note that  $\equiv\text{Fe}_w$  and  $\equiv\text{Fe}_s$  represent weak and strong sorption sites, respectively.

**Table 2.** Initial and Boundary Geochemical Conditions Used for Model Comparison.

<b>Species</b>	<b>Units</b>	<b>Boundary concentration (<math>\mathbf{x = 0, t}</math>)</b>	<b>Initial concentration (<math>\mathbf{x &gt; 0, t = 0}</math>)</b>
DOC	$\mu\text{mol l}^{-1}$	3000	0
O <sub>2</sub>	$\mu\text{mol l}^{-1}$	100	100
N(V)	$\mu\text{mol l}^{-1}$	200	200
S(VI)	$\mu\text{mol l}^{-1}$	300	300
U(VI)	$\mu\text{mol l}^{-1}$	0.1	0.1
Ferrihydrite	$\mu\text{mol dm}^{-3}$	0	50
Pyrolusite	$\mu\text{mol dm}^{-3}$	0	25
pH		6.5	6.5

**Table 3.** Transport Conditions Used in Simulations.

	Units	Value for <i>Wang et al.</i> [2003] comparison	Value for dual porosity simulations
Groundwater velocity, $v^a$	$\text{m y}^{-1}$	10	10
Dispersivity, $a^a$	M	0.25	0.25
Mobile region porosity, $\theta_m$	$\text{m}^3\text{m}^{-3}$	0.35 <sup>a</sup>	Varies <sup>b</sup> , see text
Immobile region porosity, $\theta_i$	$\text{m}^3\text{m}^{-3}$	0	Varies <sup>b</sup> , see text
Mobile-immobile mass transfer, $\gamma^c$	$\text{y}^{-1}$	0	1900 (high value) 278 (mean value) 1.8 (low value)
$\Delta x$	m	0.25	0.25

<sup>a</sup>*Wang et al.* [2003].

<sup>b</sup>*Fetter* [1994]; *Griffioen et al.* [1998]; *Kim and Corapcioglu* [2002]; *Haws et al.* [2005]; *Roden and Scheibe* [2005].

<sup>c</sup>Mass transfer values calculated from the porosity values listed and lumped porosity-mass transfer terms reported in the literature [*Feehley et al.*, 2000; *Harvey and Gorelick*, 2000; *Kim and Corapcioglu*, 2002; *Haws et al.*, 2004, 2005; *Jørgensen et al.*, 2004; *Luo et al.*, 2005; *Roden and Scheibe*, 2005].

**Table 4.** Microbial Parameter Values Used in all Simulations.

Parameter	Value	Units
$\mu_{\text{O}_2}$	0.1	$\text{mol l}^{-1} \text{y}^{-1}$
$\mu_{\text{NO}_3}$	0.004	$\text{mol l}^{-1} \text{y}^{-1}$
$\mu_{\text{Mn}}$	0.001	$\text{mol l}^{-1} \text{y}^{-1}$
$\mu_{\text{Fe}}$	0.0005	$\text{mol l}^{-1} \text{y}^{-1}$
$\mu_{\text{U}}$	0.0002	$\text{mol l}^{-1} \text{y}^{-1}$
$\mu_{\text{SO}_4^{2-}}$	0.017	$\text{mol l}^{-1} \text{y}^{-1}$
$\mu_{\text{CO}_2}$	0.05	$\text{mol l}^{-1} \text{y}^{-1}$
$K_{\text{DOC}}$	54	$\mu\text{mol l}^{-1}$
$K_{\text{O}_2}$	20	$\mu\text{mol l}^{-1}$
$K_{\text{NO}_3}$	20	$\mu\text{mol l}^{-1}$
$K_{\text{Mn}}$	3.7	$\mu\text{mol l}^{-1}$
$K_{\text{Fe}}$	3.7	$\mu\text{mol l}^{-1}$
$K_{\text{U}}$	0.1	$\mu\text{mol l}^{-1}$
$K_{\text{SO}_4^{2-}}$	10	$\mu\text{mol l}^{-1}$
$\chi_{\text{O}_2}$	0.5	$\mu\text{mol l}^{-1}$
$\chi_{\text{NO}_3}$	6	$\mu\text{mol l}^{-1}$
$\chi_{\text{Mn}}$	1	$\mu\text{mol l}^{-1}$
$\chi_{\text{Fe}}$	5	$\mu\text{mol l}^{-1}$
$\chi_{\text{SO}_4^{2-}}$	15	$\mu\text{mol l}^{-1}$



**Table 5.** Initial and Boundary Geochemical Conditions Used for Simulations.

<b>Species</b>	<b>Units</b>	<b>Boundary concentration (<math>x = 0, t</math>)</b>	<b>Initial concentration (<math>x &gt; 0, t = 0</math>)</b>
DOC	$\mu\text{mol l}^{-1}$	3000	0
O <sub>2</sub>	$\mu\text{mol l}^{-1}$	200	0
N(V)	$\mu\text{mol l}^{-1}$	200	200
S(VI)	$\mu\text{mol l}^{-1}$	300	300
U(VI)	$\mu\text{mol l}^{-1}$	1	1
Ferrihydrite	$\text{mmol dm}^{-3}$	0	0.16
Pyrolusite	$\text{mmol dm}^{-3}$	0	0.03
Calcite	$\text{mmol dm}^{-3}$	0	0.80
Calcium	$\text{mmol l}^{-1}$	3.5	0
Carbonate	$\text{mmol l}^{-1}$	1	1
pH		6.5	6.5



















