KINETIC MODELING OF MICROBIALY-DRIVEN REDOX CHEMISTRY OF RADIONUCLIDES
IN SUBSURFACE ENVIRONMENTS: COUPLING TRANSPORT, MICROBIAL METABOLISM
AND GEOCHEMISTRY

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ABSTRACT

Microbial degradation of organic matter is a driving force in many subsurface geochemical systems, and therefore may have significant impacts on the fate of radionuclides released into subsurface environments. In this paper, we present a general reaction-transport model for microbial metabolism, redox chemistry, and radionuclide migration in subsurface systems. The model explicitly accounts for biomass accumulation and the coupling of radionuclide redox reactions with major biogeochemical processes. Based on the consideration that the biomass accumulation in subsurface environments is likely to achieve a quasi-steady state, we have accordingly modified the traditional microbial growth kinetic equation. We justified the use of the biogeochemical models without the explicit representation of biomass accumulation, if the interest of modeling is in the net impact of microbial reactions on geochemical processes. We then applied our model to a scenario in which an oxic water flow containing both uranium and complexing organic ligands is recharged into an oxic aquifer in a carbonate formation. The model simulation shows that uranium can be reduced and therefore immobilized in the anoxic zone created by microbial degradation.

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Introduction

Microorganisms are ubiquitous in subsurface environments. Microbially-mediated redox reactions have been documented in various subsurface environments (e.g., Baedeker and Back, 1979a, 1979b; Frind et al., 1990; Chapelle, 1993; Fish, 1993; Jakobsen and Postma, 1994; Kent et al., 1994; Vroblecky and Chapelle, 1994; Brlke and Denver, 1995; Chapelle et al., 1995; Cozzarelli et al., 1995; Essaid et al., 1995; Heron and Christensen, 1995). Microbial degradation of organic matters, derived either naturally or from human activity, is a driving force in many subsurface geochemical systems (e.g., Chapelle, 1993). Microbial reactions are thus expected to have significant impacts on the fate of radionuclides released into subsurface environments. First of all, microorganisms can directly mediate the redox reactions of multi-valent radionuclide such as uranium and plutonium (e.g., Francis et al., 1991). Second, the biodegradation of organic carbon and the resulting inorganic processes directly determine the overall pore water chemistry including pH, carbonate concentrations, and redox conditions (Van Cappellen and Wang, 1996a) and thus control the solubility of radionuclides. Third, the biodegradation process induces the intensive dissolution and precipitation of authigenic Mn and Fe minerals and thus controls the availability of mineral phases capable of scavenging radionuclides (Van Cappellen and Wang, 1996a; Hunter et al., 1998). Fourth, biodegradation may eliminate organic ligands that can potentially complex with radionuclides, thus reducing the mobility of radionuclides. Furthermore, microbial cells may act as colloidal particles and therefore facilitate radionuclide transport (Gillow et al., 1999). Clearly, an appropriate approach to model radionuclide transport in a subsurface system must take into account the major biogeochemical processes in subsurface environments and the coupling of heavy metals with those processes.

Various reaction-transport models have been developed in recent years to model redox chemistry of subsurface systems (e.g., MacQuarrie et al., 1990; McNab and Narasimhan, 1994; Essaid et al., 1995; Lichtner, 1996; Steefel and Yabusaki, 1996; Hunter et al., 1998). Hunter et al. (1998) developed a kinetic approach to model the coupled transport, microbial metabolism, and geochemical processes. This approach allows us, on one hand, to include critical details of biogeochemical dynamics of

subsurface systems and, on the other hand, to simplify the chemical systems by focusing only on the measurable geochemical parameters without considering the details of microbial growth dynamics. In this paper, we extend this approach to explicitly include biomass accumulation and the interactions of radionuclides with major biogeochemical processes.

Kinetics of Organic Carbon Degradation and Biomass Accumulation

Assume that there are n_{DOC} dissolved organic compounds and n_{SOC} solid organic compounds available for microbial degradation in a subsurface system. Each organic compound can be degraded sequentially through six reaction pathways, depending on the availability of electron acceptors (O_2 , NO_3^- , Mn(IV), Fe(III), and SO_4^{2-}) (Van Cappellen and Wang, 1996b; Wang and Van Cappellen, 1996). The reaction pathways include aerobic respiration, denitrification, Mn(IV) reduction, Fe(III) reduction, sulfate reduction, and methanogenesis, which can be described by combining reactions (1-2) with reactions (3-8) in Table 1. We further assume that the microorganisms responsible for biodegradation can be roughly divided into six groups (aerobes, denitrifiers, Mn(IV) reducers, Fe(III) reducers, sulfate reducers, and methanogens), each corresponding to an individual degradation pathway. Using the multiple Monod formulation (Molz et al., 1986; Essaid et al., 1995), the degradation rate of organic compound i via the j -th reaction pathway can be expressed by:

$$R_{ij}^{DOC} = \frac{k_{ij}^{DOC} [DOC_i]}{K_{ij}^{DOC} + [DOC_i]} P_j f_j \quad (1)$$

$$R_{ij}^{SOC} = \frac{k_{ij}^{SOC} [SOC_i]}{K_{ij}^{SOC} + [SOC_i]} P_j f_j \quad (2)$$

where R_{ij}^{DOC} is the degradation rate of dissolved organic compound i via the j -th reaction pathway; R_{ij}^{SOC} the degradation rate of solid organic compound i via the j -th reaction pathway; $[DOC_i]$ is the molarity of dissolved organic compound i ; $[SOC_i]$ is the concentration of solid organic compound i (mole/dm³ of bulk sediment); the

concentration; k_{ij}^{DOC} is the maximum specific utilization rate of the dissolved organic compound; k_{ij}^{SOC} is the maximum specific utilization rate of the solid organic compound; K_{ij}^{DOC} and K_{ij}^{SOC} are the half-saturation constants; P_j is the active biomass of the j -th group microorganisms; and f_j characterizes the activity of the j -th group microorganisms.

Using the formulation proposed by Van Cappellen and Wang (1996b), the activity of the j -th group microorganisms can be calculated as follows:

$$f_0 = 0$$

$$\text{for } j = 1, 2, \dots, 5$$

$$f_j = \left(1 - \sum_{l=1}^{j-1} f_l \right) \frac{[EA_j]}{K_j^{EA} + [EA_j]} \quad (4)$$

$$f_6 = 1 - \sum_{l=1}^5 f_l \quad (5)$$

where $[EA_j]$ is the concentration of electron acceptor j ; K_j^{EA} is a half-saturation constant characterizing the limiting effect of electron acceptor concentration on the j -th degradation pathway.

When the active biomass is being grown and sustained by organic carbon degradation, the biomass accumulation of the j -th group microbes can be calculated by:

$$R_j^{syn} = \sum_i \phi Y_{ij}^{DOC} R_{ij}^{DOC} + \sum_i Y_{ij}^{SOC} R_{ij}^{SOC} - b_j P_j^n \quad (6)$$

where R_j^{syn} is the rate of biomass accumulation of the j -th group microorganisms; Y_{ij}^{DOC} and Y_{ij}^{SOC} are the cell yield coefficients; and b_j is the specific death rate; and ϕ is the porosity. Y_{ij}^{DOC} and Y_{ij}^{SOC} depend on the energetics of individual reaction pathways and can be estimated from the Gibbs free energy changes of the reactions (Criddle et al., 1991). For a given organic carbon substrate, the cell yield coefficient seems to decrease from a more energetically-favorable reaction pathway (e.g., aerobic respiration) to a less energetically-favorable reaction pathway (e.g. methanogenesis) (Criddle et al., 1991). Equation (6) is derived from a widely-used biomass growth equation (Criddle et al., 1991; Essaid et al., 1995; Rittmann and VanBriesen, 1996) with a modification to the biomass decay term ($b_j P_j^n$), the last term on the right side of equation (6). The

modification is based on the consideration of the achievement of a stable microbial population under steady state chemical conditions (See Appendix).

The rate of electron production in biodegradation pathway j can be calculated by:

$$R_j^e = \phi \sum_i R_{ij}^{DOC} (4a_i^D + b_i^D - 2c_i^D - 3d_i^D) + \sum_i R_{ij}^{SOC} (4a_i^S + b_i^S - 2c_i^S - 3d_i^S) - 20R_j^{sym} \quad (7)$$

where the biomass is assumed to be $C_5H_7O_2N$ (Criddle et al., 1991). The released electrons are directly used to reduce various electron acceptors through primary reduction reactions (3-8) in Table 1. Therefore, the rates of the primary reduction reactions (R_i^{pr}) are determined by:

$$R_j^{pr} = \frac{1}{e_j} R_j^e \quad i = 1, 2, \dots, 6 \quad (8)$$

Quasi-Steady State Analysis for Biomass Accumulation

It is expected that on a typical time scale for subsurface geochemical systems microbial communities have sufficient time to adapt to any natural environment. This is particularly true for a steady state geochemical system, such as those in deep-water sediments where chemical fluxes have remained constant for a long time. For simplicity, let's consider a subsurface system with one dissolved organic carbon substrate. From Equation (6), the steady state of biomass accumulation implies:

$$\frac{dP_j}{dt} = R_j^{sym} = Y_j^{DOC} R_j^{DOC} - b_j P_j^n = 0 \quad (9)$$

Combining it with equation (1), we obtain:

$$P_j = \left\{ \frac{Y_j^{DOC} k_j^{DOC} [DOC_i] f_j}{K_j^{DOC} + [DOC_i] b_j} \right\}^{\frac{1}{n-1}} \quad (10)$$

and

$$R_j^{DOC} = \left\{ \frac{Y_j^{DOC}}{b_j} \right\}^{\frac{1}{n-1}} \left\{ \frac{k_j^{DOC} [DOC_i] f_j}{K_j^{DOC} + [DOC_i]} \right\}^{\frac{n}{n-1}} \quad (11)$$

Equation (10) indicates that biomass accumulation is not an independent variable in a quasi-steady state system. Therefore, this justifies the use of the biogeochemical models

without the explicit representation of biomass, if the modeling interest is mainly on the net impact of microbial reactions on geochemical processes. This type of model actually has been successfully applied to various biogeochemical systems (e.g., Wang and Van Cappellen, 1996). But, in a case where our interest is in biocolloid-facilitated radionuclide transport, biomass accumulation has to be considered explicitly. Equation (10) then allows us to calculate biomass accumulation as a function of organic carbon substrate and electron acceptors. Furthermore, equation (11) shows that for $n > 2$ and a low concentration of organic substrate, the first order kinetics may be sufficient for describing organic carbon degradation.

Kinetics of Secondary Redox Reactions and Mineral Dissolution/Precipitation

The oxidation of organic compounds produces the reduced species Mn^{2+} , Fe^{2+} , NH_4^+ , H_2S , and CH_4 , which may become re-oxidized, as they are transported into more oxic zones (Table 1). Secondary redox reactions play an important role in overall subsurface redox cycles (Wang and Van Cappellen, 1996; Hunter et al., 1998). In low temperature environments, local chemical equilibria among redox couples are usually not achieved, and the redox conditions can not be defined by a unique Eh value (Stumm and Morgan, 1981; Siegel et al., 1991; Lindberg and Runnells, 1984; Kent et al., 1994). Therefore, the traditional equilibrium approach of using redox potential (Eh) is not adequate for predicting the redox behavior of radionuclides in a subsurface system. A kinetic approach must be employed. Bimolecular kinetic laws are used to describe the dependence of the rate of a secondary redox reaction (R_j^{sr}) on the concentrations of oxidant and reductant (Van Cappellen and Wang, 1996b):

$$R_j^{sr} = k_j^{sr} [\text{oxidant}][\text{reductant}] \quad (12)$$

where [...] denote the concentration of either oxidant or reductant; k_j^{sr} is the reaction rate constant.

Non-redox mineral dissolution/precipitation reactions (Table 1) have to be included, in order to predict pore water chemistry. These reactions are driven by the degree of saturation of the pore water with respect to the mineral involved. The rate of

non-redox mineral precipitation is described by (Wang et al., 1994; Van Cappellen and Wang, 1996b):

$$R_i^m = \begin{cases} k_i^m(\Omega_i - 1) & \text{for } \Omega_i \geq 1 \\ k_{-i}^m[Q_i^m](\Omega_i - 1) & \text{for } \Omega_i < 1 \end{cases} \quad (13)$$

where R_i^m is the mineral precipitation rate; k_i^m and k_{-i}^m are the apparent rate constants; Ω_i is the degree of saturation of pore water with respect to the mineral; Q_i^m is the content of the mineral in sediments.

Coupling Radionuclide Reactions with Major Biogeochemical Processes

In this section, we use uranium as an example to demonstrate how to couple radionuclide reactions with major biogeochemical processes. This coupling is fulfilled by U reactions listed in Table 2. A multi-valent radionuclide such as U(VI) can be directly reduced by microorganisms (e.g., Francis et al., 1991). This reduction seems to take place in zones dominated by Fe reduction, sulfate reduction, and methanogenesis. For simplicity, we assume the rate of this reduction (R_{HM}^{Pr}) to be proportional to the rate of the appropriate primary reduction reactions and the concentration of dissolved U(VI):

$$R_{HM}^{Pr} = \eta [\sum U(VI)] \sum_{j=h}^6 R_j^{Pr} \quad (14)$$

where η is a proportionality constant. For U(VI), the reduction seems to start in the Fe(III) reduction zone; therefore, the h in the above equation can be set to 4. Using a similar treatment for major element reactions, the rates of all secondary redox reactions and mineral dissolution/precipitation for U are described by Equations (12) and (13), respectively. All aqueous speciation reactions for U are assumed to be in equilibrium. Reaction (43) in Table 2 is included in order to investigate the effect of organic ligand degradation on radionuclide complexation.

The adsorption substrates for radionuclides in a microbially-driven subsurface redox system can be grouped into three categories, each with a distinct adsorption coefficient: (1) Mn and Fe oxyhydroxides, (2) Mn(II) and Fe (II) carbonate minerals, and (3) background minerals. The Mn and Fe oxyhydroxides and carbonates are expected to

vary greatly in quantity along the flow path of a contaminant plume, due to microbial reactions (Hunter et al., 1998). We here assume all adsorption reactions to be reversible. For instance, the amount of UO_2^{2+} adsorbed on Mn and Fe oxyhydroxides, $[\equiv S - UO_2^+]$, can be calculated by:

$$K_{ad} = \frac{[\equiv S - UO_2^+][H^+]}{[\equiv S - H][UO_2^{2+}]} \quad (15)$$

where K_{ad} is the equilibrium constant of adsorption reaction (34) in Table 2; the symbol of " $\equiv S -$ " denotes the surface complexation sites. The total number of adsorption sites (TS) on Mn and Fe oxyhydroxides is determined by:

$$TS = \theta \{ [MnO_2] + [FeOOH] \} = [\equiv S - H] + [\equiv S^-] + [\equiv S - UO_2^+] + \dots \quad (16)$$

where θ is the density of adsorption sites on Mn and Fe oxyhydroxides.

During the formation of authigenic minerals, especially Mn and Fe oxyhydroxides and carbonate minerals, the adsorbed radionuclide may be partly incorporated into the bulk structures of the authigenic minerals, a process called coprecipitation. The amount of heavy metal coprecipitated is expected to be proportional to both the amount of radionuclide adsorbed and the host mineral precipitation rate. In the reverse process, when the authigenic minerals dissolve, the coprecipitated radionuclides are released back into pore water. The release rate is controlled by the dissolution rate of the host minerals. We adopt the following rate expression to describe the heavy metal coprecipitation and release:

$$R_{HM}^{cpp} = \begin{cases} \lambda R_{host}^{ppt} [HM^{ad}] / [Total \text{ adsorption sites}] & \text{for } R_{host}^{ppt} > 0 \\ R_{host}^{ppt} [HM^{cpp}] / [Host] & \text{for } R_{host}^{ppt} \leq 0 \end{cases} \quad (17)$$

where R_{HM}^{cpp} is the rate of heavy metal coprecipitation with a particular host mineral; R_{host}^{ppt} is the precipitation rate of the host mineral; $[HM^{ad}]$ and $[HM^{cpp}]$ are the concentrations of heavy metal adsorbed on and coprecipitated with the host mineral; $[Host]$ is the concentration of the host mineral; and λ is the proportional constant with $0 < \lambda < 1$.

Model Simulation

The above modeling scheme has been incorporated into the computer code BIORXNTRN Version 2.0 (Hunter et al., 1998). In this section, we use the code to simulate a scenario in which an oxic water flow containing both uranium and complexing organic ligands is recharged into an oxic aquifer in a carbonate formation. The modeling results are presented in Figures 1 and 2. Along the flow path, the incoming oxic water first becomes anoxic due to microbial degradation, forming an anaerobic zone, and then become re-oxidized when it mixes with original oxidized groundwater. The Fe and Mn oxyhydroxides contained in the sediment are reductively dissolved in the anaerobic zone. Coupled with major element (C, Mn, Fe) reactions, U(VI) is reduced both directly by microbes and by the reduced species such Fe^{2+} , forming UO_2 mineral in the anaerobic zone. U adsorption is strongly correlated with the distribution of Mn and Fe oxyhydroxides. Due to the strong complexation of UO_2^{2+} with CO_3^{2-} , the effect of adsorption on U retardation is insignificant, compared to the reductive precipitation. The simulation shows the presence of organic carbon can create an anoxic zone along the flow path, which can significantly immobilize radionuclides such as uranium and plutonium.

In this paper, we have established a general framework for modeling radionuclide migration in a microbially-mediated subsurface geochemical system. It needs to be pointed out that the use of this type of model is currently limited by lack of appropriate kinetic data. Nevertheless, our model provides a tool for conducting a sensitivity analysis of a subsurface system to clarify controlling geochemical factors. The parameterization of the model against field data allows us to constrain model input parameter data.

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Appendix

The following chemical kinetics is widely used for describing biomass accumulation (Criddle et al., 1991; Essaid et al., 1995; Rittmann and VanBriesen, 1996):

$$\frac{dX}{dt} = R^{sm} = Y \frac{kS}{K + S} X - bX \quad (A1)$$

where R^{sm} is the biomass accumulation rate; Y is the cell yield coefficient; X is the active biomass concentration; k is the maximum specific utilization rate of the substrate; K is the half-saturation constant; and b is the specific death rate.

We postulate that in many subsurface biogeochemical systems active microbial populations are likely to achieve a steady state. Then, the limitation of equation (A1) becomes apparent. The equation is not able to generate a steady state solution, i.e., when the left side of the equation approaches zero, the biomass concentration (X) becomes undefined. To overcome this limitation, we suggest modifying equation (A1) to:

$$\frac{dX}{dt} = R^{sm} = Y \frac{kS}{K + S} X - bX^n \quad (A2)$$

with $n > 1$ to ensure that the stable biomass concentration is proportional to the concentration of the limiting substrate.

Table 1. Irreversible major element reactions identified to be important for modeling heavy metal transport in subsurface redox systems.

Organic carbon oxidation:

Primary reduction

Secondary redox reaction

Non-redox mineral precipitation

Table 2. List of uranium chemical reactions included in model calculations

Primary reduction

Secondary redox reaction

Non-redox mineral dissolution/precipitation

Sorption

Aqueous speciation

Figure 1A

Figure 1B

Figure 1C

Figure 1D

Figure 1. Concentration changes of major elements along the flow path. The biogeochemical reactions of major elements (C, O, N, Mn, Fe, and S) control the overall chemical environments for radionuclide migration.

Figure 2A

Figure 2B

Figure 2. Concentration changes of uranium species along the flow path. U(VI) is immobilized within the anoxic zone induced by microbial reactions.