

Simulating Bioremediation of Uranium-Contaminated Aquifers

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Abstract

Bioremediation of trace metals in groundwater may require the manipulation of redox conditions via the injection of a carbon source. To simulate the numerous biogeochemical processes that will occur during the bioremediation of trace-metal-contaminated aquifers, a reactive transport model has been developed. The model consists of a set of coupled mass balance equations, accounting for advection, hydrodynamic dispersion, and a kinetic formulation of the biological or chemical transformations affecting an organic substrate, electron acceptors, corresponding reduced species, and trace metal contaminants of interest, uranium in this study. The redox conditions of the domain are characterized by estimating the pE, based on the concentrations of the dominant terminal electron acceptor and its corresponding reduced specie. This pE and the concentrations of relevant species are then used by a modified version of MINTEQA2, which calculates the speciation/sorption and precipitation/dissolution of the species of interest under equilibrium conditions. Kinetics of precipitation/dissolution processes are described as being proportional to the difference between the actual and calculated equilibrium concentration.

keywords: bioremediation, groundwater, modeling, uranium.

1. Introduction

The fate of trace metals in the subsurface is affected by many biogeochemical interactions with a variety of organic/inorganic chemical species and minerals under different redox conditions. These interactions can affect the mobility of contaminants by altering physical and chemical characteristics such as their speciation, sorption, and solubility. *In situ* stimulation of microbially mediated redox reactions has drawn significant attention as a potentially safe and cost-effective strategy for remediating trace-metal contaminated aquifers. In recent years, various models have been developed that included biologically mediated redox dynamics in terms of the sequential utilization of different electron acceptors during the degradation of an organic substrate [Van Cappellen and Wang, 1995]. Some of these models have been extended to include abiotic redox reactions and geochemical processes such as speciation and precipitation/dissolution [Wang and van Cappellen, 1996; Hunter et al., 1998; Smith, and Jaffé, 1998]. Based on these biological and geochemical processes, trace metals dynamics in groundwater have been described by several authors. Non-equilibrium conditions

of surrounding geochemistry have been implemented in formulating the cycling of minerals [Hunter et al., 1998], and in the formulation of the dynamics of trace metals and it has been assumed the metals are driven kinetically towards chemical equilibrium [Smith and Jaffé, 1998].

Aqueous phase homogeneous reactions such as speciation, complexation, or acid-base reactions are usually described as instantaneous reactions because they are very fast reactions compared to the change in concentration due to groundwater transport. In contrast, biologically mediated reactions and heterogeneous reactions such as precipitation/dissolution are relatively slow and have been incorporated by several authors into transport models using kinetic relationships.

2. Model Development

Throughout the redox profile that develops in subsurface environments, various processes such as reduction/oxidation, sorption/desorption, precipitation/dissolution, and/or the formation of complex ions can affect the fate of trace metals directly or indirectly. A system of mass balance equations was formulated for the dissolved and solid species of interest in a saturated porous medium:

$$\text{dissolved species:} \quad (1 + K_i^{eff}) \frac{\partial(\phi C_i^{aq})}{\partial t} = \nabla \cdot (\mathbf{D}_{h_i} \cdot \nabla(\phi C_i^{aq})) - \nabla \cdot (v(\phi C_i^{aq})) + \sum R_i \quad (1)$$

$$\text{mineral phase:} \quad \frac{\partial}{\partial t} [(1 - \phi) C_j^s] = - \sum R_j \quad (2)$$

Where C_i^{aq} and C_j^s are the concentrations of the dissolved species i and the mineral phase j ;

\mathbf{v} is the groundwater velocity vector; \mathbf{D}_{h_i} is the hydrodynamic dispersion tensor of dissolved species i ; $\sum R_i$ and $\sum R_j$ are the net consumption/production rates of the dissolved species i and the mineral phase j by geochemical reactions; ϕ is the porosity; K_i^{eff} is an effective partition coefficient for the equilibrium adsorption of species i . Due to substantial amounts of external carbon sources supplied into the contaminated aquifer during biostimulation, the rate of biodegradation of the dissolved organic substrate can be formulated using a dual-Monod kinetics as [Smith and Jaffé, 1998]:

$$R_C^{bio} = - \sum_{eA}^{N_{eA}} \chi_{v,eA} \mu_{m,eA} \left(\frac{C_C}{K_{s,C} + C_C} \right) \left(\frac{C_{eA}}{K_{s,eA} + C_{eA}} \right) \quad (3)$$

Where N_{eA} is the number of terminal electron acceptors considered; C_C and C_{eA} are the concentrations of the dissolved organic substrate and a given terminal electron acceptor. $\chi_{v,eA}$ is an indicator coefficient for the utilization of a terminal electron acceptor, which is determined by the concentration of the precedent terminal electron acceptor. $\mu_{m,eA}$ is the electron-acceptor-dependent rate of organic substrate oxidation. $K_{s,eA}$ and $K_{s,C}$ are the half-saturation coefficients for the electron acceptor and the organic substrate, respectively.

The rate of consumption of a given terminal electron acceptor and the production of its corresponding reduced species are formulated as:

$$R_{eA}^{bio} = -\chi_{eA} \alpha_{eA} \mu_{m,eA} \left(\frac{C_C}{K_{s,C} + C_C} \right) \left(\frac{C_{eA}}{K_{s,eA} + C_{eA}} \right) = -R_{\text{corresponding reduced species}}^{bio} \quad (4)$$

Where α_{eA} is the stoichiometric coefficient. The rate of oxidation of ammonia and the production of nitrate and the oxidation of methane as well as corresponding consumption of oxygen are also represented by a Monod-type expression. The reduced species that are being produced in the process of the biodegradation of the organic substrate, as well as NH_4^+ and CH_4 can be re-oxidized when they are transported into a more oxidizing region. The rate of oxidation of dissolved reduced species i by dissolved oxidant j is formulated by second-order rate expressions as:

$$R_{i,j}^{abio} = -\mu_{i,j} C_i C_j \quad (5)$$

Where $\mu_{i,j}$ is the second order rate coefficient for the abiotic reaction between species i and j . An analogous formulation is applied for the rate of oxidation of adsorbed Fe(II) and Mn(II) by dissolved oxygen, which is represented as a function of the concentration of the reduced metal adsorbed onto manganese or iron oxides and dissolved oxygen concentration:

$$R_{M^{2+},O_2}^{abio} = \mu_{M^{2+},O_2} [XO_2 \cdot M^{2+}] \cdot C_{O_2} \quad (6)$$

Where μ_{M^{2+},O_2} is the rate coefficient for the oxidation of the adsorbed metal M^{2+} ; $[XO_2 \cdot M^{2+}]$ is the concentration of this same metal, adsorbed onto metal oxides XO_2 . This adsorbed concentration is calculated either using the double layer complexation module of MINTEQA2, or by using an effective partition coefficient specified as a model input.

3. Model Application and Discussion

Under oxidizing conditions the dominant form of uranium is U(VI) as in the oxide UO_3 and/or the yellow uranyl ion UO_2^{2+} which are highly soluble and mobile, while under reducing conditions uranium forms insoluble phases such as urinite and/or coffinite in the form of U(IV). Complexation of U(VI) with carbonates is accounted for in the model when the lumped partition coefficients are estimated based on the computed speciation of the different species in solution.

The reduction of U(VI) can be caused by biotic/abiotic reactions. Some Fe(III)- and sulfate-reducing bacteria are capable of reducing uranium under anaerobic conditions by using U(VI) as a terminal electron acceptor during the oxidation of organic substrates. Based on thermodynamic energy yield, uranium reduction should occur in the sequence of $\text{Mn(IV)} > \text{U(VI)} > \text{Fe(III)}$. Since U(VI) is an electron acceptor with a relatively low concentration, we assumed that after Mn(IV) is used up, biotic U(VI) reduction occurs simultaneously with

Fe(III) reduction, and may continue simultaneously with sulfate reduction. U(VI) can also be reduced via abiotic reactions such as by Fe(II) sorbed onto iron corrosion products like hematite. On the other hand, U(IV) can be oxidized to U(VI) in the presence of oxygen or nitrate. The consumption/production of U(VI) and U(IV) is described as:

$$\sum R_{U6} = \mu_{O,U4} (1-\phi) C_O C_{U4} - \chi_{Fe3} \alpha_{U6} \mu_{m,U6} \frac{C_{U6}}{K_{s,U6} + C_{U6}} \frac{C_C}{K_{s,C} + C_C} - \mu_{U6,Fe2(ad)} K_{d,Fe2}^{eff} \phi C_{Fe2} C_{U6} \quad (7)$$

$$\sum R_{U4} = \frac{\phi}{1-\phi} \left(\chi_{Fe3} \alpha_{U6} \mu_{m,U6} \frac{C_{U6}}{K_{s,U6} + C_{U6}} \frac{C_C}{K_{s,C} + C_C} + \mu_{U6,Fe2(ad)} K_{d,Fe2}^{eff} \phi C_{Fe2} C_{U6} \right) - \phi \mu_{O,U4} C_O C_{U4} \quad (8)$$

Where $\mu_{m,C,U6}$ is the maximum rate of organic substrate oxidation with U(VI) as the electron acceptor. $\mu_{O,U4}$ and $\mu_{U6,Fe2(ad)}$ are the second order rate coefficient for the abiotic reactions of oxygen/U(IV) and U(VI)/sorbed Fe(II), respectively. $K_{d,Fe2}$ is the partition coefficient of Fe(II). A series of numerical experiments were conducted to assess the dynamics of uranium in a saturated aquifer during bioremediation. Prior to biostimulation, it was assumed that the aquifer is contaminated by U(VI) with a concentration of 0.1 mmol/L. A series of electron acceptors with specified concentration were assumed to exist in the system. Upstream constant concentration boundary conditions were set, which were equal to the initial conditions for all constituents except for the dissolved organic substrate. The solid-phase bioavailable Mn(IV) and Fe(III) were set to their respective initial concentrations which were constant throughout the domain at $t = 0$.

Figure 1 shows the simulated concentration profiles of the different electron acceptors, and Figure 2 that of the reduced species, one year after a carbon source was injected at the origin. As soon as the organic substrate is introduced at the upstream boundary it is biodegraded using the available electron acceptor, which gradually changes the domains redox conditions from oxidizing to reducing.

The effect of the aquifer biostimulation via the injection of the carbon source on U(VI) reduction can be seen in Figure 3. After the carbon source is injected at the origin, the U(VI) concentration steadily decreases. The concentration of U(IV) increases significantly as time progresses at about 1m from the origin. The reason is that at this distance, and for the conditions simulated, oxygen and nitrate as well as the initial amount of Mn(IV) have all been utilized in the degradation of the organic substrate, allowing the utilization of U(VI) to start at this point, which then precipitates as U(IV). Furthermore, since no oxidants reach the zone where the U(VI) precipitated, the precipitate remains stable and is not reoxidized into U(VI). No biological uranium reduction takes place until all the Mn(IV) has been consumed, Figure 3 indicates that U(IV) can be found near the origin where more favorable electron acceptors still exist. The presence of U(IV) in this zone is due to the abiotic reduction of U(VI) by sorbed Fe(II). As opposed to the major electron acceptors described in the model, U(VI) reduction was allowed to proceed in parallel with the reduction of the other electron acceptors after Mn(IV) has been consumed. For this reason U(VI) reduction proceeds even when the environment becomes highly reduced and methanogenesis occurs. Further research is necessary to establish if there is a lower redox limit for the reduction of U(VI).

4. Conclusion

This study presents a numerical model for simulating the biogeochemical dynamics of trace metals in saturated porous media under biostimulation via the injection of a carbon source. Redox profiles during the biodegradation of the organic substrate were simulated and coupled with the dynamics of uranium in order to illustrate the biological reduction of U(IV) and in situ immobilization of U(VI). Chemical equilibrium calculations are performed to determine the local deviation from equilibrium conditions. The deviation from equilibrium conditions is then used to formulate a kinetic expression that drives the system towards equilibrium conditions. These reaction kinetics can have significant impacts on the individual chemical profiles. When the water flow is from the oxidized zone to the reduced zone, the electron acceptors are depleted sequentially in the order of thermodynamic energy yield. Conversely, when the water flows from reduced to more oxidized zones, the various biotic and abiotic reactions occurring simultaneously can alter the spatial sequence of the profiles of the electron acceptors. This, as well as the overlapping concentration profiles, illustrates that knowledge of the electron acceptor profiles alone does not provide adequate information to identify the zones where a specific microbiological process is occurring. Additional measurements might be required to assess what degradation process is occurring at a given location.

5. References

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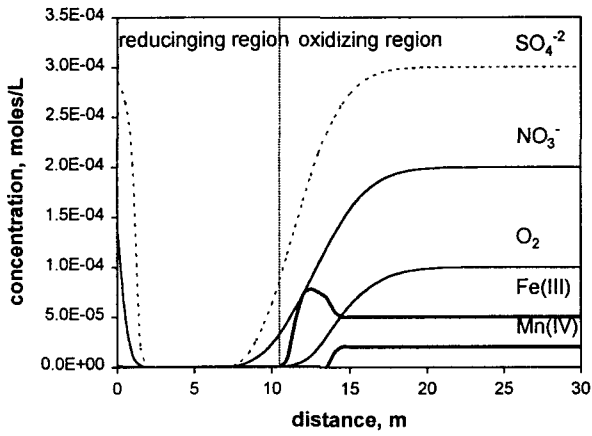


Figure 1. Simulated concentration profiles of terminal electron acceptors after 1 year of biostimulation

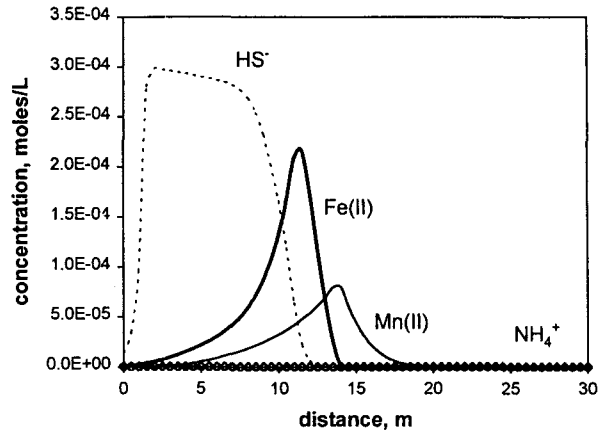


Figure 2. Simulated concentration profiles of reduced species after 1 year of biostimulation

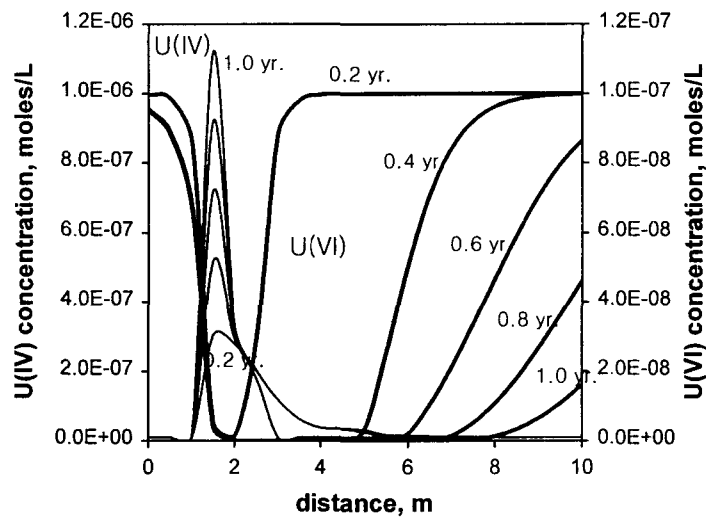


Figure 3. Simulated concentration profiles of U(IV) and U(VI) over 1 year of biostimulation