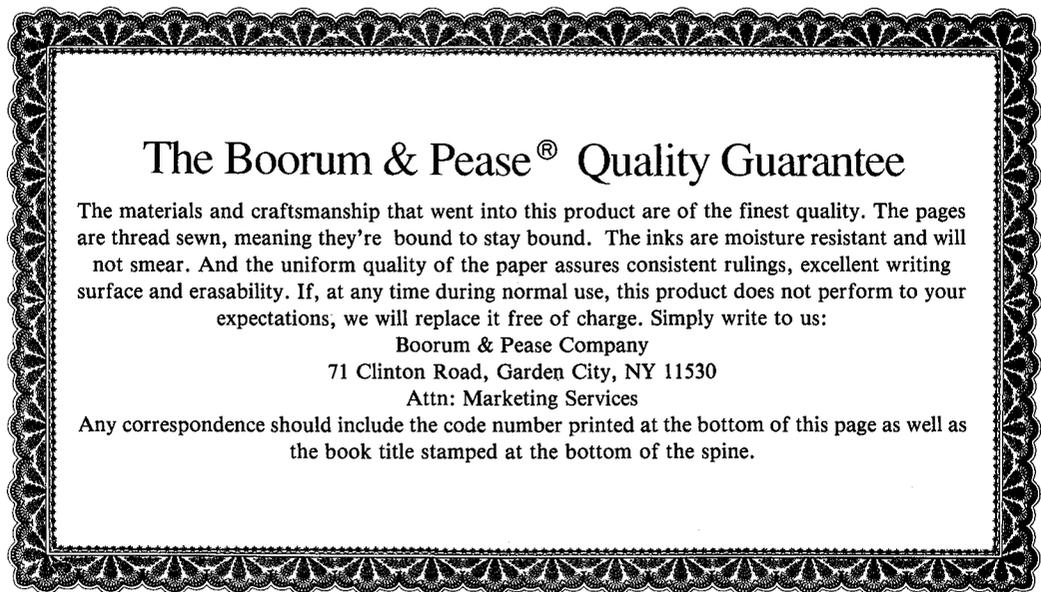


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Scientific Notebook #146 for
Subregional Hydrogeology
Research Project

Scientific Notebook for "Subregional
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20-5704-176



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Contents

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Entries will be made by: Ross Baptzopolou
of pasted electronic copies of Peter Lichtner's
notes.

3.2.6 Task 6: Site-Scale Flow and Transport Modeling

3.2.6.1 Objectives

This task has three main objectives. The first is to evaluate the applicability of the SUFLAT methodology to simulate groundwater flow processes (e.g., vapor-phase transport, geothermal and diurnal thermal gradients, etc.) considered plausible at the YM site. As a result of this evaluation, the methodology may be enhanced, as appropriate. After all possible modifications have been implemented, a number of sensitivity studies will be conducted in order to study the future hydrologic behavior of YM under different rates of infiltration and evapotranspiration. The second is to investigate the different transport behavior of various alternative models of coupled flow and transport (e.g., discrete fracture, equivalent versus stochastic continuum versus dual-porosity, conservative versus reactive transport). The third is to investigate the role of heterogeneities in creating and amplifying preferential flow paths resulting from elevated temperatures around the repository.

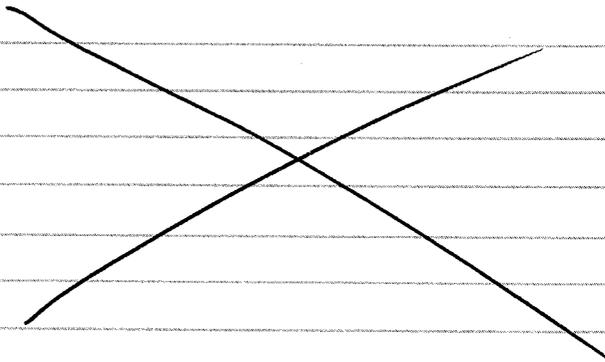
3.2.6.2 Justification

To perform a critical license application review, the NRC staff needs an assessment of the groundwater flow and transport processes considered plausible at the YM site. Coupling multiphase water movement, heat transfer, and gas flow models with stochastic and/or geostatistical models will allow a critical evaluation of these processes under parameter uncertainty. The synergistic effects of coupling complex flow and transport processes with heterogeneous properties may be profound and currently are not well understood.

3.2.6.3 Task Description

Task 6 will have a four year duration and comprises the following activities.

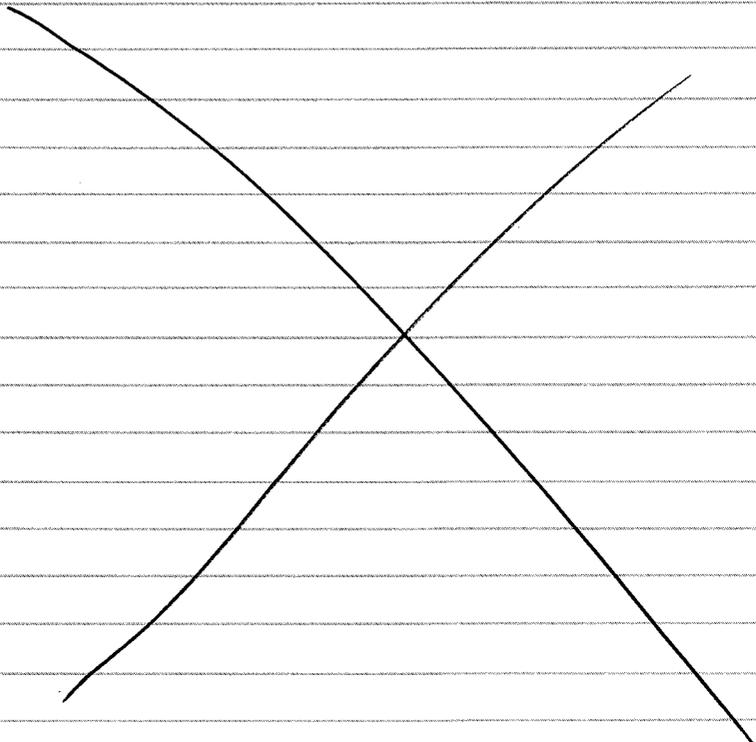
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OBJECTIVE

Reactive transport simulations for the YM or ALTS will be conducted, accounting for geochemical interactions such as aqueous speciation, sorption, and mineral precipitation/dissolution reactions. The calculations will make use of flow fields established in Subtask 6.1. 1D simulations will be carried out along streamlines in the flow fields. It is proposed to use the code GEM (and possibly MPATH) for the reactive transport calculations. Currently both GEM and MPATH apply to fully saturated conditions and will need to be modified for unsaturated flow. The code GEM provides for advective/diffusive and dispersive transport in a single spatial dimension. It accounts for a variety of chemical reactions including aqueous speciation, mineral precipitation/dissolution, sorption, and electrochemical migration. In its present form, however, the solvent water is presumed to be in abundance and is not explicitly considered. The fluid velocity is set by an external parameter and is held constant. Modifications to GEM necessary for carrying out this task include adding Darcy's law for fluid transport and constitutive relations, such as the van Genuchten relationships, describing partially saturated porous media. In addition, it will be necessary to add a two-phase fluid flow component to model vapor transport. These modifications will be an activity shared between this project and the EBS element, with most of the developmental work being conducted under the auspices of the EBS element.

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2. Sub-Regional Hydrology Processes: Site-Scale Flow & Transport Modeling

Account Number: 20-5704-176

Collaborators: Ross Bagtzoglou

Objective: The purpose of this work is to modify the code GEM to include partially saturated porous media.

Date Entry

4.15.95

K_D 's: WHAT DO THEY MEAN AND WHEN CAN WE USE THEM?
Notes on Retardation and Reactive Transport

ABSTRACT

The question of the use of K_D 's is analyzed from the point of view of reactive mass transport. Specifically the question of when a constant retardation factor can be used in modeling is discussed. The question of charge balance is discussed in regard to surface complexation models.

INTRODUCTION

Several difficulties arise when combining batch calculations of distribution coefficients with reactive transport. The batch value corresponds to the local value within a REV. It may or may not be constant.

CONCENTRATION VARIABLES

Concentration variables are defined for a single REV. Each REV is characterized by the pore volume V_p and solid volume V_s with

$$V = V_p + V_s. \quad (2-5)$$

[2-1]

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In addition mole numbers for the j th aqueous and adsorbed species, n_j , \bar{n}_j , respectively, define the composition of the aqueous and solid phases. In terms of these quantities the following quantities can be defined:

$$\text{aqueous concentration: } C_j = \frac{n_j}{V_p}, \quad (2-6)$$

$$\text{sorbed concentration: } \bar{C}_j = \frac{\bar{n}_j}{V}, \quad (2-7)$$

$$\text{distribution coefficient: } K_j^D = \frac{\bar{n}_j}{n_j} = \frac{\bar{n}_j}{V} \cdot \frac{V}{V_p} \cdot \frac{V_p}{C_j} = \frac{\bar{C}_j}{\phi C_j}, \quad (2-8)$$

$$\text{cation exchange capacity: } Q_{ex} = \frac{\bar{n}_{ex}}{m_{solid}} = \frac{\bar{n}_{eq}}{V} \cdot \frac{V}{V_s} \cdot \frac{V_s}{m_{solid}} = \frac{\bar{w}}{\rho_s(1-\phi)}, \quad (2-9)$$

$$\text{bulk density: } \rho_{bulk} = \frac{m_s}{V} = \frac{m_s}{V_{solid}} \cdot \frac{V_{solid}}{V} = \rho_s(1-\phi), \quad (2-10)$$

where the total number of moles of sorbed sites equal to

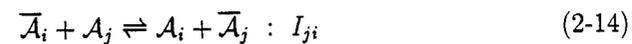
$$\bar{n}_{ex} = \sum_j z_j \bar{n}_j, \quad (2-11)$$

$$\bar{w} = (1-\phi)\rho_s Q_{ex}, \quad (2-12)$$

and

$$\rho_{bulk} = (1-\phi)\rho_s. \quad (2-13)$$

MONO VALENT EXCHANGE



$$K_{ij} = \frac{C_i}{\bar{C}_i} \cdot \frac{\bar{C}_j}{C_j} \quad (2-15)$$

$$K_{ij} = \frac{k_j}{k_i} \quad (2-16)$$

$$\bar{C}_j = \frac{k_j C_j}{k_i C_i} \bar{C}_i \quad (2-17)$$

[2-2]

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$$\sum_j \bar{C}_j = \bar{w}. \quad (2-18)$$

$$\bar{C}_j = \frac{\bar{w} k_j C_j}{\sum_i k_i C_i} \quad (2-19)$$

$$K_j^D = \frac{\bar{C}_j}{\phi C_j} = \frac{\bar{w} k_j}{\sum_i k_i C_i} \quad (2-20)$$

MASS TRANSPORT EQUATIONS

$$\frac{\partial}{\partial t} \phi C_j + \frac{\partial J_j}{\partial x} = -\sum_{i \neq j} I_{ji}, \quad (2-21)$$

$$\frac{\partial \bar{C}_j}{\partial t} = \sum_{i \neq j} I_{ji}. \quad (2-22)$$

Alternatively

$$\frac{\partial}{\partial t} [\phi C_j + \bar{C}_j] + \frac{\partial J_j}{\partial x} = 0. \quad (2-23)$$

$$\frac{\partial}{\partial t} [\phi(1+K_j^D)C_j] + \frac{\partial J_j}{\partial x} = 0. \quad (2-24)$$

$$\frac{\partial}{\partial t} [\phi R_j C_j] + \frac{\partial J_j}{\partial x} = 0, \quad (2-25)$$

where the retardation factor R_j is defined by

$$R_j = 1 + K_j^D. \quad (2-26)$$

An alternative definition of the distribution coefficient is

$$\tilde{K}_j^D = \frac{\bar{n}_j/m_s}{n_j/V_p} = \frac{V_p}{V} \cdot \frac{V}{m_s} \cdot \frac{\bar{n}_j}{n_j} = \frac{\phi}{\rho_{bulk}} K_j^D. \quad (2-27)$$

With this definition the retardation factor becomes

$$R_j = 1 + \frac{\rho_{bulk}}{\phi} \tilde{K}_j^D. \quad (2-28)$$

[2-3]

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The transport equation may be rewritten in the form

∂/∂t [φCj] + ∂Jj^R/∂x + φCj ∂ln Rj/∂t + Jj/Rj ∂ln Rj/∂x = 0, (2-29)

where Jj^R refers to the retarded flux defined as

Jj^R = Jj/Rj = -φ D ∂C/∂x + v/Rj Cj. (2-30)

5.11.95 Alteration of MINTEQ to printout Kd's directly.

MINTEQ was altered to directly printout Kd's, both in dimensionless form and in the standard units of mL/g. The results for uranium sorption on goethite is shown below in Figure 2-3. The calculations were compared with and without carbonate species present.

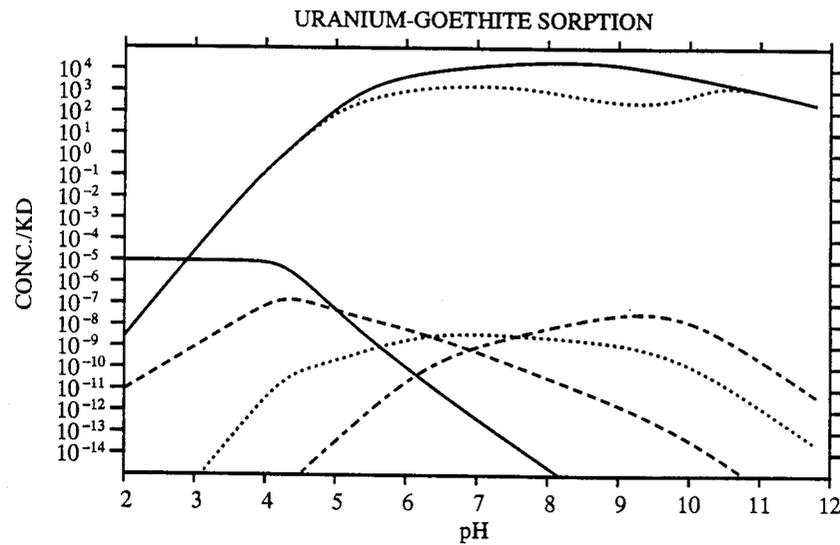


Figure 2-3: Sorption of uranium on goethite.

The upper solid curve corresponds to the retardation without carbonate species present and the upper dashed curve with carbonate species. The lower curves correspond to the concentrations of various uranium-bearing carbonate species.

The input file used in the calculation is listed below which includes carbonate species.

U(VI)-Goethite Sorption; Hsi and Langmuir (1985); No CO2; U(VI)=1E-5
DLM; XOUO2(OH)2-; 12/17/92 CNWRA database
25.00 molal 0.000 0.00000e-01

0 0 1 0 0 0 0 1 1 1 5 3
activity 330 99
0.1
hsiugoad.xyp 893 8931400 8931401 8931402 8931404

4 1 7
1.000E+00 50.00 0.000 0.000 81
330 0.000E-03 -2.00 y /H+1
813 0.000E-01 0.00 y /ADS1PSIo
811 1.918E-04 -3.72 y /ADS1TYP1
140 1.000E-03 -3.72 y /CO3-2
893 1.000E-05 -5.00 y /UO2+2
500 1.000E-01 -1.00 y /Na+1
492 1.000E-01 -1.00 y /NO3-1

3 1
330 2.0000 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo

2 3
8113300 XO- 0.0000 -9.1700 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 XOH2+ 0.0000 7.3500 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8118930 XOUO2(OH)2- 0.0000 -10.1900 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 5 1.000 811 1.000 893 2.000 2 -3.000 330 -1.000 813 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0

7.8.95

COMBINING SURFACE COMPLEXATION MODELS WITH MASS TRANSPORT

INTRODUCTION

Of fundamental concern to evaluating the suitability of Yucca Mountain, Nevada, as a potential repository for high-level nuclear waste (HLW) is the possibility of release of radionuclides from the waste package and their migration to the accessible environment as dissolved constituents in groundwater. One important

mechanism for retarding radionuclide migration is sorption on mineral surfaces. This contribution discusses some of the complications that result from combining sorption reactions with a time-space description of solute transport by advection, diffusion and dispersion coupled to homogeneous aqueous reactions and heterogeneous mineral precipitation/dissolution reactions.

Several sorption models are currently in use including ion-exchange and surface complexation models. Surface complexation models have been used to model sorption of metal ions and ligands over a wide range of chemical conditions. The more sophisticated formulations of surface complexation models provide for incorporation of the electric double layer. These models are based on the hypothesized formation of surface complexes at the mineral-solution interface analogous to the formation of aqueous complexes. Because of the difficulty in identifying species complexes on mineral surfaces, surface complexes generally serve more as fit parameters than as actual physical species.

A fundamental difficulty which arises when combining surface complexation models with mass transport is maintaining electric neutrality in the aqueous solution. Although in a closed static system electroneutrality is maintained, in an open system involving diffusive and advective transport an aqueous solution that is initially electrically neutral may not remain so as the system evolves in time. This effect of charge imbalance does not occur with ion-exchange models because for each ion sorbed, an equal amount of charge is desorbed and released into solution. Hence the aqueous solution always remains electrically neutral. This need not be the case, however, with surface complexation models. The cause of charge imbalance in these models results from the variable number of occupied surface sites which in general changes with time and distance.

APPLICATION OF SURFACE COMPLEXATION MODELS TO SORPTION OF Np^{5+} AND U^{6+}

The geochemical speciation code MINTEQA2 (Allison et al., 1991) has been developed to implement several different types of surface complexation models. Based on the assumed analogy between reactions at the mineral-water interface and aqueous complexation reactions in the bulk solution, MINTEQA2 uses mass action and mass balance constraints to calculate the distribution of a given con-

taminant between the sorbed and aqueous phases. For the purposes of HLW disposal, the MINTEQA2 thermodynamic database has been modified at CNWRA to include equilibrium constants for actinides and other radionuclides (Turner, 1993). Surface complexation model parameters, determined based on batch sorption experimental data, are also available for a number of radionuclide-mineral systems (Turner, 1995). Output format from MINTEQA2 was modified slightly to directly compute and print sorption in terms of the linear sorption coefficient (K_d in mL/g) that is commonly used in performance assessment transport calculations.

MINTEQA2 was used to calculate sorption of U^{6+} and Np^{5+} on goethite in a batch system over a range in pH. The Diffuse-Layer surface complexation model was used (Allison et al., 1991), and the assumed surface reactions and their binding constants are given in Table 1. Other model conditions are given in Table 2. In this preliminary analysis, the complete groundwater chemistry at Yucca Mountain is not considered, but a relatively dilute system has been assumed, similar to the ionic strength of water from well J-13. The results for the batch distribution coefficients for uranium and neptunium are shown in Figure 1 plotted as a function of pH ranging from 2 to 12. For both actinide-goethite systems, sorption is strongly affected by pH, increasing with increasing pH to a maximum, and then declining slightly at higher pH. For the U^{6+} -goethite system, the sorption maximum is reached at pH 6 to 7, while the calculated sorption maximum for Np^{5+} -goethite is at a higher pH (9 to 10). Over most of the pH range considered, sorption on goethite is typically several orders of magnitude greater for U^{6+} as compared to Np^{5+} . Calculated U^{6+} -goethite sorption is also more strongly affected by pH, with K_d increasing by about 9 orders of magnitude from pH 2 to 7, as compared to a 5 order of magnitude increase in the K_d for Np^{5+} -goethite.

Table 2-2: Surface complexation reactions for sorption of uranium and neptunium on goethite.

reaction	Log K
$>\text{FeOH} + \text{H}^+ \rightleftharpoons >\text{FeOH}_2^+$	9.17
$>\text{FeOH} - \text{H}^+ \rightleftharpoons >\text{FeO}^-$	-7.35
$>\text{FeOH} + \text{UO}_2^{2+} + 2\text{H}_2\text{O} - 3\text{H}^+ \rightleftharpoons >\text{FeOUO}_2(\text{OH})_2^-$	10.19
$>\text{FeOH} + \text{NpO}_2 \rightleftharpoons >\text{FeOHNpO}_2^+$	5.21

Table 2-3: Model Conditions

solid concentration	1 g/L
site density	2.31 sites/nm ²
surface area	50 m ² /g
total site concentration	1.918 × 10 ⁻⁴ moles sites/L
ionic strength	0.001 M NaCl
total U ⁶⁺ , Np ⁵⁺	10 ⁻⁷ M
pH	2-12

The introduction of carbon into a batch system has been shown by experiment to reduce actinide sorption at higher pH (e.g., Hsi and Langmuir, 1985). The current modeling also predicts reduced actinide sorption in the presence of carbonate. The conceptual model used here does not invoke the formation of any actinide-carbonate surface complexes (Table 1), and relies on the formation of aqueous actinide complexes with carbonate over much of the pH range considered to effectively compete with the mineral surface. For the U⁶⁺-goethite system, the formation of strong uranyl-carbonate complexes (Figure 2a) reduces the predicted K_d by about an order of magnitude over much of the pH range (about 4 to 10). As the uranyl carbonate species decrease at higher pH (>10.5) relative to the more hydrolyzed uranyl species UO₂(OH)₃ and UO₂(OH)₄²⁻, the predicted sorption for carbon-free and carbonate systems converge. Calculated sorption for Np⁵⁺-goethite is also reduced in the presence of carbon, but by much less than for the U⁶⁺-goethite system. This is due to the lack of a strong Np⁵⁺-carbonate complex (Figure 2b). For example, the concentration of NpO₂CO₃ does not become significant until a relatively high pH, and only becomes a dominant aqueous species over a relatively narrow pH range (9 to 10). As can be seen from the figures the K_d predicted from the surface complexation model is highly dependent on the solution composition.

Radionuclide Sorption on Goethite

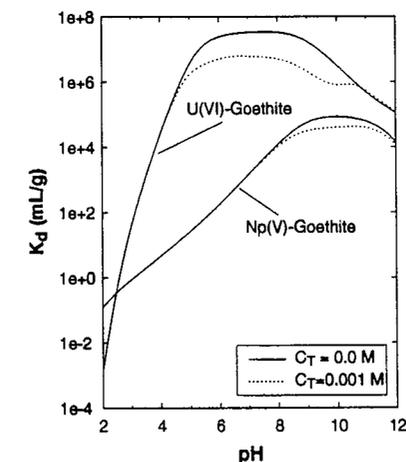


Figure 2-4: Logarithm of the distribution coefficient for sorption of uranium and neptunium on goethite plotted as a function of pH with (dashed curve) and without (solid curve) CO₂ present.

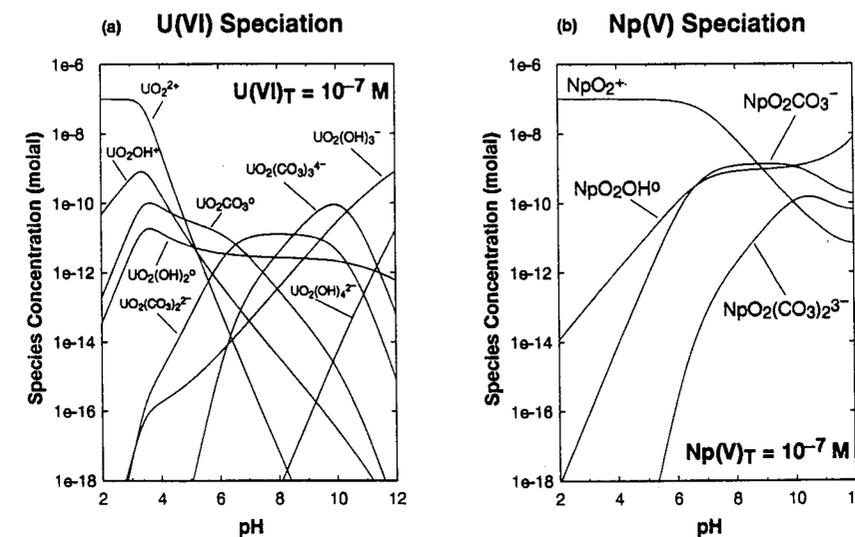
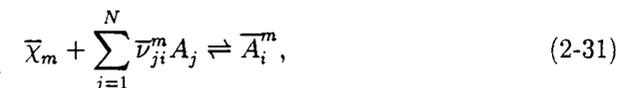


Figure 2-5: Logarithm of the concentration of selected (a) uranium- and (b) neptunium-bearing species plotted as a function of pH.

COMBINING SORPTION REACTIONS WITH MASS TRANSPORT

Incorporating sorption reactions in mass transport equations leads to the spatial separation of different solute species resulting from their relative affinity to the sorbate known as chromatography. Sorption fronts may be self-sharpening or self-broadening depending on the shape of the sorption isotherm. An added complication is caused by the changing number and types of surface sites as minerals dissolve and precipitate. Surface site concentrations are inextricably tied to mineral abundances. An intrinsic surface area, usually expressed in $\text{m}^2 \text{g}^{-1}$ or $\text{m}^2 \text{mol}^{-1}$, can be associated with each mineral. The surface contains a known site density expressed as moles of sites per meter squared. Then knowing the concentration of each mineral the site concentration can be computed. Multisite surface complexation reactions may be formulated as follows



where $\bar{\chi}_m$ denotes the neutral surface site associated with the m th mineral, $\bar{\nu}_{ji}^m$ refers to the stoichiometric coefficients, and \bar{A}_i^m the i th adsorbed surface species on the m th mineral site. In what follows an overscore is used to designate quantities referred to the mineral surface. Examples of these reactions are presented in Table 2-2 for sorption of uranium and neptunium on goethite with \bar{A}_i^m identified with $\text{>FeOUO}_2(\text{OH})_2^-$ and $\text{>FeOUO}_2(\text{OH})_2^-$, and $\bar{\chi}_m$ with >FeOH .

The number of surface sites corresponding to the m th mineral is given by the equation

$$\bar{C}_s^m = \bar{C}_{\bar{\chi}_m} + \sum_i \bar{C}_i^m. \quad (2-32)$$

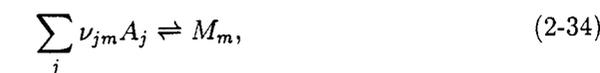
The total number of available surface sites is related to intrinsic properties of the particular mineral and proportional to the amount of mineral present. By considering a representative elemental volume (REV) containing n_m moles of the m th mineral with surface area A_m and volume V_m , and \bar{n}_s^m moles of surface sites, it follows that

$$\bar{C}_s^m = \frac{\bar{n}_s^m}{V_{\text{REV}}} = \frac{\bar{n}_s^m A_m n_m V_m}{A_m n_m V_m V_{\text{REV}}} = \frac{\eta_s^m A_m}{V_m} \phi_m, \quad (2-33)$$

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where C_j^m denotes the concentration of available sorption sites per unit volume V_{REV} of bulk porous medium, η_m refers to the site density in units of moles of sites m^{-2} , \bar{V}_m represents the molar volume, and A_m represents the intrinsic surface area in $\text{m}^2 \text{mol}^{-1}$. Note that according to this expression the site concentration is proportional to the instantaneous mineral concentration $\bar{V}_m^{-1} \phi_m$. Thus no allowance is made for covering already occupied sites by a precipitation layer, for example. In addition as a mineral dissolves surface sites are replaced by new ones, it is assumed that the dissolution process is slow to the rate of adsorption and the new sites are instantaneously occupied by sorbing ions. Similar transport equations hold for the multisite case as compared with the single site case formulated above, with an additional sum over the different sites occurring in the primary species transport equations.

If in addition to sorption, mineral precipitation/dissolution reactions take place described by the irreversible reactions



for mineral M_m with stoichiometric coefficients ν_{jm} , the mass transport equations referred to a porous medium with porosity ϕ have the following form (Lichtner, 1985):

$$\frac{\partial}{\partial t} (\phi \Psi_j) + \nabla \cdot \Omega_j = - \sum_m \nu_{jm} I_m - \sum_i \bar{\nu}_{ji} \bar{I}_i, \quad (2-35)$$

for the j th primary species,

$$\frac{\partial \bar{C}_i}{\partial t} = \bar{I}_i, \quad \frac{\partial \bar{C}_{\bar{\chi}}}{\partial t} = - \sum_i \bar{I}_i, \quad (2-36)$$

for the i th sorbed species and the concentration of empty surface sites. In these equations Ψ_j refers to the total generalized concentration of the j th primary species and Ω_j the generalized flux defined by (Lichtner, 1985)

$$\Psi_j = C_j + \sum_i \nu_{ji} C_i, \quad \Omega_j = J_j + \sum_i \nu_{ji} J_i = (-\phi D \nabla + v) \Psi_j, \quad (2-37)$$

where C_j denotes the concentration of the j th primary species and C_i denotes the concentration of the i th reversible aqueous complex with stoichiometric reaction coefficients ν_{ji} , with J_i the individual species flux, D the diffusion/dispersion

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coefficient assumed to be the same for all species, and fluid flow velocity v , \bar{C}_i denotes the concentration of the i th surface complex, \bar{C}_x denotes the concentration of empty sites, I_m refers to the rate of the m th mineral reaction, and \bar{I}_i refers to the rate of the adsorption reaction. The total number of sorption sites must be conserved by the transport equations.

CHARGE CONSERVATION

To investigate the ability of various sorption models to conserve charge when combined with solute transport, two distinct models are considered: ion-exchange and surface complexation. First a two-component system is considered involving the sorption of Na^+ and Ca^{2+} .

Ion-Exchange

Ion-exchange of Na^+ with Ca^{2+} is described by the reaction



in which charge is conserved separately in both the aqueous and surface phases. In this reaction X^- denotes a surface site. Representing the rate of the exchange reaction by I_{ex} , the following transport equations hold:

$$\hat{\mathcal{L}}[\text{Na}] = 2I_{\text{ex}}, \quad \hat{\mathcal{L}}[\text{Ca}] = -I_{\text{ex}}, \quad (2-39)$$

for the aqueous species Na^+ and Ca^{2+} with their corresponding concentrations denoted by the square brackets $[\dots]$, where $\hat{\mathcal{L}}$ denotes the differential operator

$$\hat{\mathcal{L}} = \phi \frac{\partial}{\partial t} + v \frac{\partial}{\partial x} - \phi D \frac{\partial^2}{\partial x^2}. \quad (2-40)$$

In this simple example possible aqueous complexing reactions are omitted. This does not, however, affect the utility of the example regarding charge conservation. It follows immediately that for the ion-exchange reaction charge in the aqueous solution is conserved. The total charge density in solution contributed by cations is equal to

$$Q = [\text{Na}] + 2[\text{Ca}]. \quad (2-41)$$

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Electroneutrality is achieved by an equal and opposite contribution from anions. Because the anion transport equations are not coupled to the cation transport equations, in order for the solution to remain electrically neutral, both sets of transport equations must conserve charge individually. Therefore only the cations need be explicitly considered in what follows. It follows that

$$\hat{\mathcal{L}}Q = \hat{\mathcal{L}}[\text{Na}] + 2\hat{\mathcal{L}}[\text{Ca}] = 2I_{\text{ex}} - 2I_{\text{ex}} = 0. \quad (2-42)$$

As a consequence of this equation charge is conserved and the aqueous solution will remain electrically neutral with increasing time if it is electrically neutral initially.

Surface Complexation Model

For sorption models with a variable number of unoccupied sites, however, charge is not in general conserved. Consider the following surface complexation reactions:



with rates I_{Na} and I_{Ca} , respectively, where X^- denotes a negatively charge surface site and XNa and X_2Ca represent sorbed species. The mass transport equations read:

$$\hat{\mathcal{L}}[\text{Na}] = -I_{\text{Na}}, \quad \hat{\mathcal{L}}[\text{Ca}] = -I_{\text{Ca}}. \quad (2-44)$$

For the sorbed species and unoccupied sites

$$[\dot{\text{XNa}}] = I_{\text{Na}}, \quad [\dot{\text{XCa}}] = I_{\text{Ca}}, \quad [\dot{\text{X}}] = -I_{\text{Na}} - 2I_{\text{Ca}}. \quad (2-45)$$

It follows that the total number of sites is conserved, as they must:

$$\omega_{\text{X}} = [\dot{\text{X}}] + I_{\text{Na}} + 2I_{\text{Ca}} = 0, \quad \text{with} \quad \omega_{\text{X}} = [\text{X}] + [\text{XNa}] + 2[\text{X}_2\text{Ca}]. \quad (2-46)$$

However, total charge within the aqueous solution is not conserved:

$$\hat{\mathcal{L}}Q = -I_{\text{Na}} - 2I_{\text{Ca}} = [\dot{\text{X}}] \neq 0. \quad (2-47)$$

Thus the nonconservation of charge in the surface complexation model is directly related to the rate of change with time of the unoccupied site density.

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Multicomponent System

This result can be extended easily to the general case of a multicomponent system. To demonstrate that the transport equations do not necessarily conserve charge, first note that the primary species transport equations Eqn.(2-35) can be simplified by eliminating the sorption reaction rates \bar{I}_i , yielding the equivalent transport equations

$$\frac{\partial}{\partial t} \left(\phi \Psi_j + \sum_i \bar{\nu}_{ji} \bar{C}_i \right) + \nabla \cdot \Omega_j = - \sum_m \nu_{jm} I_m. \quad (2-48)$$

The transport equation for conservation of charge can be derived by multiplying these equations by the valence z_j of the j th primary species and summing over all primary species to give

$$\frac{\partial}{\partial t} \left(\phi Q + \sum_{ij} z_j \bar{\nu}_{ji} \bar{C}_i \right) + \nabla \cdot \Omega_Q = 0, \quad (2-49)$$

where the total charge in solution Q and current density Ω_Q are defined by

$$Q = F \sum_j z_j \Psi_j, \quad \text{and} \quad \Omega_Q = F \sum_j z_j \Omega_j = (-\phi D \nabla + v) Q. \quad (2-50)$$

The right hand side of Eqn.(2-49) vanishes because mineral precipitation/dissolution reactions, as all chemical reactions, conserve charge. The second term in brackets on the left-hand side of Eqn.(2-49) represents the total charge on the surface. Referring to this quantity as \bar{Q} it follows that

$$\bar{Q} = F \sum_{ji} z_j \bar{\nu}_{ji} \bar{C}_i = F \sum_i \bar{z}_i \bar{C}_i. \quad (2-51)$$

With this definition, Eqn.(2-49) can be expressed as

$$\frac{\partial}{\partial t} (\phi Q) + \nabla \cdot \Omega_Q = - \frac{\partial \bar{Q}}{\partial t}. \quad (2-52)$$

Charge is conserved only if the right-hand side of this equation vanishes identically. However, surface charge alone is *not* conserved in surface complexation models as it is in ion-exchange models. For example in the electric double layer model, surface charge plus the charge contained within the diffuse layer is conserved. This suggests that one way to correct for nonconservation of charge is

to include in the mass transport equations the contribution from nonspecific adsorbed ions contained in the diffuse layer. For the simpler surface complexation models which do not explicitly include the double layer, there does appear to be any way to conserve charge when these models are combined with solute transport.

ELECTRIC DOUBLE LAYER MODEL

The deficiency in the surface complexation model to conserve charge when combined with mass transport equations can be rectified by explicitly taking into account in the mass conservation equations the electric double layer and the contribution of nonspecific adsorbed ions in the diffuse layer.

The concentration of ions in the diffuse layer is presumed to be related to the bulk concentration through the Boltzmann factor by the expression

$$C_i^{\text{dl}}(x) = C_i e^{-z_i F \psi(x) / RT}, \quad (2-53)$$

where C_i^{dl} denotes the concentration of the i th species with valence z_i within the diffuse layer, the coordinate x represents the distance from the charged surface, C_i denotes the bulk concentration of the i th species, F denotes the Faraday constant, ψ the electric double layer potential, R the gas constant, and T the temperature. The concentration of adsorbed species is obtained from the mass action equations corresponding to Eqn.(2-31) leading to the expression

$$\bar{C}_i^m = \bar{K}_i^m C_{\bar{x}_m} \prod_{j=1}^N (\gamma_j C_j P_0^{z_j})^{\bar{\nu}_{ji}^m} = \bar{K}_i^m C_{\bar{x}_m} P_0^{\bar{z}_i} \prod_{j=1}^N (\gamma_j C_j)^{\bar{\nu}_{ji}^m}, \quad (2-54)$$

where C_j denotes the bulk concentration of the j th primary species, and the factor P_0 is given by the Boltzmann distribution

$$P_0 = e^{-F \psi_0 / RT}, \quad (2-55)$$

where ψ_0 the electric double layer potential evaluated at the surface. The latter expression is obtained noting that the valence associated the the i th adsorbed species \bar{z}_i is related to the valencies of the primary species by the equation

$$\bar{z}_i = \sum_j \bar{\nu}_{ji} z_j. \quad (2-56)$$

From the expression for the total number of surface sites corresponding to the m th mineral given by the equation

$$\bar{C}_s^m = \bar{C}_{\bar{x}_m} + \sum_i \bar{C}_i^m = \bar{C}_{\bar{x}_m} \left\{ 1 + \sum_i \bar{K}_i^m P_0^{\bar{z}_i} \prod_{j=1}^N (\gamma_j C_j)^{\bar{\nu}_{ji}^m} \right\}, \quad (2-57)$$

and the mass action equations, Eqn.(2-54), the sorption isotherms for the concentration of empty sites and adsorbed species are given, respectively, by

$$\bar{C}_{\bar{x}_m} = \frac{\bar{C}_s^m}{1 + \sum_i \bar{K}_i^m P_0^{\bar{z}_i} \prod_{j=1}^N (\gamma_j C_j)^{\bar{\nu}_{ji}^m}}, \quad \text{and} \quad \bar{C}_i^m = \frac{\bar{C}_s^m \bar{K}_i^m P_0^{\bar{z}_i} \prod_{l=1}^N (\gamma_l C_l)^{\bar{\nu}_{li}^m}}{1 + \sum_{i'} \bar{K}_{i'}^m P_0^{\bar{z}_{i'}} \prod_{j=1}^N (\gamma_j C_j)^{\bar{\nu}_{ji'}^m}}. \quad (2-58)$$

SURFACE EXCESS CONCENTRATION

In order to formulate a transport model which has the desirable property of conserving charge, it is necessary to account for the concentration of ions within the diffuse layer. This can be accomplished by introducing the surface excess concentration defined by (Borkovec and Westall, 1983)

$$\Gamma_i^m = \int_{x_d}^{\infty} [C_i^{m,dl}(x) - C_i] dx, \quad (2-59)$$

for the m th mineral surface. The surface excess concentration may be positive or negative. Referring to a REV, the excess concentration in the diffuse layer may be expressed as

$$\delta C_i^{m,dl} = \frac{\delta n_i^m}{V_P} = \frac{\delta n_i^m A_m n_m V_m V_{REV}}{A_m n_m V_m V_{REV} V_P} = \frac{A_m \phi_m}{\phi V_m} \Gamma_i^m, \quad (2-60)$$

where δn_i^m refers to the mole excess contained in the REV. The surface excess concentration in the diffuse layer may be positive or negative.

MASS TRANSPORT EQUATIONS INCLUDING NONSPECIFIC ADSORBED IONS

Mass transport equations including the effects of adsorption and the contribution of nonspecific adsorbed ions in the diffuse layer have the form

$$\frac{\partial}{\partial t} \left[\phi (\Psi_j + \delta \Psi_j^{dl}) + \sum_i \bar{\nu}_{ji} \bar{C}_i \right] + \frac{\partial \Omega_j}{\partial x} = - \sum_m \nu_{jm} I_m, \quad (2-61)$$

where

$$\delta \Psi_j^{dl} = \sum_m \left[\delta C_j^{m,dl} + \sum_i \nu_{ji} \delta C_i^{m,dl} \right]. \quad (2-62)$$

The accumulation term in the transport equation for bulk solute species is assumed to consist of the sum of contributions from the diffuse layer, the so-called nonspecifically adsorbed species, and the bulk solution itself. However, because species in the diffuse layer are not transported in the bulk solution, they give rise to an additional retardation effect beyond that given by the specifically adsorbed species.

With this form of the transport equations charge conservation is guaranteed. Multiplying the transport equation for the j th primary species by the charge z_j and summing over all primary species yields

$$\frac{\partial}{\partial t} (\phi Q) + \nabla \cdot \Omega_Q = \frac{\partial}{\partial t} \left[\bar{Q} + F \phi \sum_j z_j \delta \Psi_j^{dl} \right]. \quad (2-63)$$

Conservation of charge in the aqueous phase thus follows from conservation of charge of adsorbed and nonspecifically adsorbed species in the diffuse layer which requires that the following relation be satisfied identically

$$\bar{Q} = -F \phi \sum_j z_j \delta \Psi_j^{dl}. \quad (2-64)$$

This condition is simply the statement that surface charge is balanced by the total charge contained within the diffuse layer.

RETARDATION

Retardation is influenced by the nonspecific sorption in the electric diffuse layer as well as specific ion adsorption on the charged surface. The local distribution coefficient giving the ratio of total concentration of adsorbed species including contributions from both the specific and nonspecific adsorbed species to the aqueous concentration can be defined as

$$\mathcal{K}_j^D = \frac{\sum_i \bar{\nu}_{ji} \bar{C}_i + \delta \Psi_j^{dl}}{\Psi_j}. \quad (2-65)$$

Without taking the ions in the diffuse layer into account results in the distribution coefficient

$$\kappa_j^{D0} = \frac{\sum_i \bar{\nu}_{ji} \bar{C}_i}{\Psi_j} \quad (2-66)$$

The ratio of the distribution coefficients with and without the contribution from nonspecific adsorbed ions is thus equal to

$$\frac{\kappa_j^D}{\kappa_j^{D0}} = \frac{\sum_i \bar{\nu}_{ji} \bar{C}_i + \delta \Psi_j^{dl}}{\sum_i \bar{\nu}_{ji} \bar{C}_i} = 1 + \frac{\delta \Psi_j^{dl}}{\sum_i \bar{\nu}_{ji} \bar{C}_i} \quad (2-67)$$

The ratio is close to unity if the contribution from nonspecific adsorbed ions is small compared to the specifically adsorbed ions. However, in general, because $\delta \Psi_j^{dl}$ may be positive or negative, κ_j^D may become negative or even vanish.

CONCLUSION

Combining sorption reactions with mineral precipitation/dissolution reactions adds new challenges to modeling reactive transport problems. Special attention needs to be given to the resulting transport equations to ensure that electroneutrality is maintained in the aqueous solution as the system evolves with time.

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