RE-EVALUATING EFFECTS OF SORPTION KINETICS ON COLLOID-ENHANCED MIGRATION OF PLUTONIUM

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ABSTRACT

Several previously published phenomenological models used for simulating the potential effects of sorption kinetics on colloid-enhanced migration of Pu at Yucca Mountain are based upon certain simplifying assumptions that are mechanistically inconsistent with the sorption behavior of the contaminant. Here, a more complex mechanistic approach that does not require such assumptions is compared with previous predictions. The new model builds upon recent research initiatives that have for the first time developed binding and kinetic constants for the individual oxidation states of Pu on mineral oxide surfaces. It retains the ability to simulate the complexity of the rate-limited sorption behavior of Pu and provides a tool for investigating the effects of important environmental variables (i.e., pH, Eh, major ion concentration, etc.) on Pu migration. Model simulations indicate previous phenomenological models may overestimate colloid migration of Pu by several orders of magnitude or more and also point out potential future environmental factors that may have greater influence on Pu migration than sorption kinetics.

INTRODUCTION

Models provide a means for predicting behavior within systems that cannot be fully characterized by experiment. Because these systems are not fully characterized – models are inherently imperfect representations of the system. Adequate predictions, however, may be possible if the behavior-controlling mechanisms within the system are identified and accurately represented.

Understanding the sorption behavior of plutonium in natural and engineered systems is key to improving current risk assessment and remedial strategies. Plutonium in natural systems may exist in four oxidation states (III-VI) simultaneously and these states migrate within ground waters as dissolved species, precipitated intrinsic colloidal species, or pseudo-colloidal species [1]. The latter represents a scenario in which dissolved or intrinsic colloidal species sorb to or collide with existing natural colloids within solution.

Characterizing the behavior and formation mechanisms of pseudo colloids is necessary before predictions of complex systems are adequate for containment design and risk assessment purposes. Existing equilibrium models are capable of relatively accurate predictions of Pu speciation in natural solutions in the absence of colloids or suspended particles [2]. Additionally, the presence of intrinsic colloidal species may be dismissed for dilute systems where the solubility of Pu oxy-hydroxides has not been surpassed anywhere along the flow-path. However, there remains a need for developing models that are able to accurately describe the complex

sorption behavior of Pu on organic and mineral oxide surfaces. This paper focuses on designing models for the latter, with special attention given to the rate-limited sorption of Pu on Fe-bearing minerals.

Numerous laboratory investigations have enhanced our understanding of the mechanisms controlling sorption of Pu onto Fe-bearing minerals [3-7 and others]. Although a strict consensus by these experts regarding the exact mechanisms of Pu sorption to Fe-bearing minerals is still lacking, interactions between dissolved Pu and the mineral surface likely involve sorbing species of more than one oxidation state and kinetically controlled, surface mediated, redox transformations [5,6,8-10]. This complex web of reactions may lead to highly non-linear sorption behavior, potentially only predictable by models that handle each important mechanism explicitly. Such a model would require information on the binding strengths for each of the oxidation states of Pu.

Colloid-enhanced migration of Pu may limit the effectiveness of natural and engineered barriers at the proposed Yucca Mountain High Level Radioactive Waste Repository [11], so factors influencing this pathway must be studied. In lieu of definitive sorption mechanisms, some modelers have opted to develop simple three phase (dissolved, colloidal, immobile solid) models based upon a phenomenological approach. One such model has been developed to investigate colloid-enhanced migration of Pu at Yucca Mountain [11]. This model (Eq.'s 1-3) simulates the rate-limited formation of Pu pseudo-colloids by defining independent "slow" and "fast" sorbing colloidal surfaces and handles competitive sorption to immobile solid phases using a retardation coefficient (R in Eq. 1).

$$R\frac{dX}{dt} = -\omega X + M_0 \varphi(t) - k_f X + k_r Y - \alpha X + \beta Z - \lambda R X \qquad \text{(Eq. 1)}$$

$$\frac{dY}{dt} = -\omega Y + k_f X - k_r Y - \lambda Y \qquad \text{(Eq. 2)}$$

$$\frac{dZ}{dt} = -\omega Z + \alpha X - \beta Z - \lambda Z \qquad \text{(Eq. 3)}$$

Here, X is the total dissolved Pu, and Y and Z are the Pu residing on "fast" and "slow" colloid sites, respectively. The forward and reverse rate constants for the "slow" and "fast" colloid sorption sites are α and β, and k_f and k_r, respectively. The turnover rate of the aquifer is ω, λ is the Pu decay rate, M_0 is the initial total Pu injected at the source, and φ is the length of time of the injection ($=\delta t$) equal to the Dirac-delta function. The retardation coefficient is equal to $1+(1-\theta)\rho K_d/\theta$, where θ is the porosity, ρ is the bulk density, and K_d is the partition coefficient and is equal to k_f/k_r.

Typically natural systems containing colloids are said to be symmetric, where the surface of the colloid is assumed to be identical to that of the immobile solid phase [12]. In near-field regions, it is also possible to have an asymmetric system where colloid and immobile phase surfaces are dissimilar. Interestingly, the model by Painter et al. [11] describes a symmetric system initially that, over time, becomes increasingly asymmetric, favoring the formation of Pu pseudo colloids over retardation by immobile solid phases.

The important simplifying assumptions used by the model shown in equations 1-3 include, the existence of only one dissolved Pu species, linear sorption to immobile solid phases represented by R, and sorption to colloid surfaces by two independent sorbing species: one near equilibrium and one kinetically controlled. Kinetic constants, α and β, were derived from experimental results by Lu et al. [7].

Obviously, the phenomenological model by Painter et al. [11] does not attempt to explicitly represent all important chemical reactions of Pu, but rather implicitly simulate the combined effects these mechanisms would have on the overall migration pattern of the contaminant. This allows the equations that represent the chemistry to be easily combined with those that govern fluid flow and solved analytically under certain boundary conditions. The disadvantage is that an implicit model may not retain any information regarding environmental influences (i.e., pH, Eh, ionic strength) of individual mechanisms. This means that the implicit model is only applicable to the system for which it is developed, at the time it was developed. Additionally, it may not be possible or appropriate to lump all influencing mechanisms together. In any case, these simplifying model assumptions should be validated. Until recently, this has not been possible.

Here valence-specific binding and kinetic constants are developed for the sorption of Pu on Fe-bearing minerals. These constants are then incorporated into a 1-D, three-phase (dissolved, colloidal, immobile solid phase) mechanistic model based upon the *PHREEQC* geochemical modeling software [13] in order to independently investigate the effects of rate-limited sorption on colloid-enhanced migration. By explicitly handling important chemical reactions, this model provides a tool for testing various simplifying assumptions of the simpler model and retains the capability for simulating behavior under a variety of environmental conditions.

METHODOLOGY

Base Model

Mechanistic models attempt to simulate the overall behavior of a contaminant by explicitly accounting for the important influences from individual chemical processes. By explicitly treating chemical reactions that are functions of major environmental variables a mechanistic approach may, in theory, be successfully applied to a wide variety of systems of interest. It is important to note that classifying a model as "mechanistic" is largely dependent upon the particular contaminant and the system to be simulated. For instance, effects of sorption on the fate and transport of contaminants are most often simulated using a partition coefficient, K_d, which is defined simply as the ratio of the contaminant concentration sorbed on a surface ($[M]_S$) to that residing in solution ($[M]_D$).

$$K_d = \frac{[M]_S}{[M]_D}$$

(Eq. 4)

While the simplifying assumptions of the K_d approach may be valid for many organic contaminants, it is not usually suitable for most metal contaminants. This type of model

certainly does not represent in an adequate manner actual sorption behavior of Pu. A mechanistic approach to predicting Pu sorption behavior requires a more complex technique.

An equilibrium model is a type of mechanistic model. Equilibrium models assume that local equilibrium is always maintained between reactants and products of a particular reaction and that this state may be defined by a mass action equation that is expressed in terms of an equilibrium constant. To solve for the equilibrium concentrations of a system, one would need to solve simultaneously a set of equations that includes mass action equations and mass balance equations. A variety of numerical approaches have been developed to solve these multi-component problems, however, they all share the common step of decreasing the number of independent variables prior to solving the set of mass action and mass balance equations [14].

The need for more capable methods of simulating sorption behavior has lead to the development of a class of equilibrium-based models called surface complexation models (SCMs). These models assume the formation of complexes with binding sites on the mineral surface is analogous to complex formation in the bulk solution. SCMs can simulate effects of environmental influences (e.g., pH) on sorption and describe complicated behavior where multiple surface species are formed by a single contaminant – model characteristics that are necessary for modeling Pu. A summary of the detailed descriptions of SCMs provided by Davis and Kent [15] and Dzombak and Morel [16] is provided here.

The sorption of metals to mineral oxide surfaces is likely dictated by electrostatic interactions between charged ions in solution and pH dependent, protonated, neutral and deprotonated binding sites at the mineral-water interface. Reactions describing the protonation and deprotonation of the mineral surface are:

$$\equiv SOH + H^+ \Leftrightarrow \equiv SOH_2^+ \tag{Eq. 5}$$
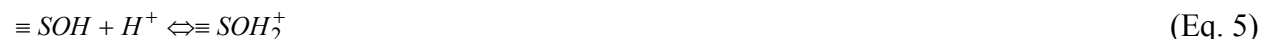
$$\equiv SOH \Leftrightarrow \equiv SO^- + H^+ \tag{Eq. 6}$$

Where $\equiv SOH$, $\equiv SOH_2^+$, and $\equiv SO^-$ represent possible neutral, positively charged and negatively charged species. Equations 5 and 6 may be defined by intrinsic (identified by *) equilibrium constants as,

$$K_+^* = \frac{\{\equiv SOH_2^+\}}{\{\equiv SOH\}\{H^+\}_S} \tag{Eq. 7}$$

And

$$K_-^* = \frac{\{\equiv SO^-\}\{H^+\}_S}{\{\equiv SOH\}} \tag{Eq. 8}$$

Where {X} indicates activities of species X equal to $\equiv SOH$, $\equiv SOH_2^+$, $\equiv SO^-$, and H^+. The only significant difference between complex formation reactions occurring at the surface with those occurring within the bulk solution is the extra work required by dissolved ions prior to formation

to travel through the potential gradient at the charged surface of the mineral. For this reason the subscript "S" is used in $\{H^+\}_S$ to indicate the activity of the hydrogen ion at the surface. The Boltzman relation can then be used to translate $\{H^+\}_S$ to the more meaningful value of $\{H^+\}$ the hydrogen ion activity within the bulk solution.

$$\{X^{+Z}\}_S = \{X^{+Z}\}\left[e^{-\psi F / RT}\right]^Z \tag{Eq. 9}$$

Where ψ (with units of C) is the electrostatic potential at the surface, F is the Faraday constant (96,485 C mol^{-1}), R is the ideal gas constant (8.3145 J K^{-1} mol^{-1}), and z is the charge of the ion. This expression for the activity of the ion at the surface may be substituted in equation 8 to relate the intrinsic equilibrium constant in terms of ion activity in the bulk solution. For the reaction represented by equations 5 and 6, the expression in terms of bulk hydrogen ion activity becomes

$$K_+^* = \frac{\{\equiv SOH_2^+\}}{\{\equiv SOH\}\{H^+\}\left[e^{-\psi F / RT}\right]^Z} \tag{Eq. 10}$$

Describing the sorption on the mineral surface of ions other than hydrogen is handled in an identical fashion. As an example, the sorption of $Pu^{VI}O_2^{+2}$ by the reaction

$$\equiv SOH + PuO_2^{2+} \Leftrightarrow \equiv SOPuO_2^+ + H^+ \tag{Eq. 11}$$

Is considered. The intrinsic equilibrium constant describing this reaction is

$$K^* = \frac{\{\equiv SOPuO_2^+\}\{H^+\}_S}{\{\equiv SOH\}\{PuO_2^{2+}\}_S} = \frac{\{\equiv SOPuO_2^+\}\{H^+\}\left[e^{-\psi F / RT}\right]}{\{\equiv SOH\}\{PuO_2^{2+}\}\left[e^{-\psi F / RT}\right]^2} = \frac{\{\equiv SOPuO_2^+\}\{H^+\}}{\{\equiv SOH\}\{PuO_2^{2+}\}\left[e^{-\psi F / RT}\right]} \tag{Eq. 12}$$

K* can be defined in terms of an apparent equilibrium constant (K^{app}) and the change on the surface (Δz) as a result of surface complexation.

$$K^* = K^{APP}\left[e^{-\psi F / RT}\right]^{-\Delta z} \tag{Eq. 13}$$

Several of the most popular SCMs are the two-layer diffuse layer model (DLM) and the constant capacitance model (CCM), and the triple layer model (TLM). These models, although similar in approach, differ in complexity with the two-layer models being the simplest and requiring the least fitting parameters. Comparisons of the three models showed each were able to fit radionuclide sorption data equally well, indicating the more complex TLM provided no measurable advantage over two-layer models. A DLM was chosen for its simplicity and comparison purposes with results generated previously [17].

One key aspect of any equilibrium model is the accuracy of equilibrium constants that are used to represent chemical behavior. The accuracy of this type of model is dependant upon whether all important equilibrium constants are included in the database, whether these constants are correct, and whether the assumption of local equilibrium is met for each reaction.

If the assumption of local equilibrium is not met for a particular reaction, a kinetic model is used to describe the progression of that reaction with time. For rates that can be described explicitly, this may be as simple as including a rate equation that expresses the rate of change of a product or reactant. In more complex systems, reaction rates may be functions of a combination of several factors, including but not limited to diffusion processes across phase boundaries, biological degradation, or radioactive decay. Complex rate equations that cannot be described explicitly must be solved numerically.

Best available formation constants were taken from the literature for each of the elements modeled in this research. The *WATEQ4F* [18] thermodynamic database was augmented with best available constants for Pu and its analogs as suggested by several extensive reviews [19-21]. Acidity constants for each of the mineral oxides considered were taken from [17,22]. A single binding site type with a constant site density equal to 2.3×10^{18} sites m^{-2} was assumed for mineral surfaces, as recommended by Dzombak and Morel [16]. Ionic strength corrections were made using the relatively simple Davies equation [13]. More complex methods for estimating activity coefficients were not warranted here since all simulations were conducted for systems at room temperature and within solutions of low (<0.1 M) ionic strength.

Regression with *INVRS K*

It may not be possible to derive constants describing sorption on natural surfaces for all of the oxidation states of Pu directly from experimental data. Derivations of these constants require the measurement of redox distributions within solution and on the surface, since Pu may exist simultaneously in four different oxidation states within aqueous solutions. While it is expected that the binding strength of Pu onto mineral surfaces may vary with oxidation state by ten orders of magnitude or more, traditional analytical techniques are only capable of detecting redox distributions to less than two orders of magnitude and may alter the redox distribution of Pu during the procedure [23]. Lacking sufficient measurements to derive constants, some researchers have assumed the dominant oxidation state of Pu on the surface was identical to that within solution [5,6,17]. However, this is only true if the dominant oxidation state within solution also maintains the highest binding strength on the mineral surface. Only when these two points are confirmed, can data from Pu sorption experiments be used effectively to develop Pu sorption constants. Alternatively, sorption constants for Pu might be derived from measured data of its redox-stable analogs without making unsubstantiated assumptions regarding Pu surface redox speciation.

The simplest method for estimating constants is to directly measure the concentrations of all species in a reaction over time (if estimating kinetic constants) or that has reached equilibrium (if estimating equilibrium constants). However, in most cases the concentrations of important species cannot be measured directly, but can be calculated using well-known equilibrium and kinetic constants and equilibrium and kinetic models. These calculations require measurement of dependent variables such as total concentrations of important components rather than concentrations of individual species. Hand calculations can be made for simple models, but computer-based tools are desirable for a complex system such as one containing unknown plutonium species.

A computer program module has been developed that integrates a Gauss-Newton nonlinear regression routine with the chemical equilibrium and kinetic modeling power of *PHREEQC* [13] to enable inverse calculations of unknown or poorly defined equilibrium and kinetic constants. This module is called *INVRS_K* [19]. *INVRS K* provides the capability to regress on unknown or poorly defined chemical equilibrium or kinetic constants from a series of experimental data. A number of unknown constants equal to or smaller than the number of dependent variables (in the form of experimental data) may be regressed upon.

A Gauss-Newton non-linear regression uses a Taylor series expansion to approximate a non-linear function in a linear form [24]. An example is used here of a simple regression based upon several dependent variables or experimental measurements used to regress on two unknown constants. The subscript "i" is used as an index to represent a particular dependent variable (D_v). Each dependent variable is a function of several unknown constants. A set of equations written in matrix form may be solved for changes in each of the unknown constants (represented as vector $\{\Delta K\}$) using the relationship described in Chapra and Canale [24]:

$$\left[[Z_l]^T [Z_l] \right] \{\Delta K\} = \left\{ [Z_l]^T \{f\} \right\}$$
(Eq. 14)

Where l is the iteration number, matrix $[Z_l]$ contains the partial derivatives of Dv_s evaluated at l, and vector $\{f\}$ contains the residuals of all datasets. New values for unknown constants can be calculated from ΔK (Chapra and Canale, 1998). The approximate relative error (ε_a) associated with each unknown constant at every iterative step may also be calculated and is equal to:

$$\left| \varepsilon_{a,i}^{l+1} \right| = \left| \frac{K_i^{l+1} - K_i^l}{K_i^{l+1}} \right| 100\%$$
(Eq. 15)

This process would be repeated until the approximate relative errors for all values of K fall below acceptable limits.

The Gauss-Newton algorithm is known to suffer from convergence problems if constants are far from their least-squares values. This is due to the fact that non-linear relationships between constants and dependent variables are approximated by linear ones. This potential problem is complicated by the fact that results produced by *INVRS K* are not only dependent upon the convergence of the numerical method used for regression but also convergence on acceptable solutions for the equilibrium or kinetic models by *PHREEQC*. However, it is the author's experience that the non-linear regression routine used by *INVRS K* is quite robust as long as convergence is obtained by the numerical method within *PHREEQC*.

Conceptual Kinetic Model for Pu Sorption to Fe-bearing Surfaces

It is rarely adequate to assume local equilibrium is maintained between all valence states of Pu when modeling its behavior in complex systems. Typically two classes of reactions, including precipitation/dissolution and redox reactions, tend not to maintain equilibrium within the environment [25]. For purposes of developing a model for simulating dilute systems, only the second class of reactions is assumed important here.

Various redox reactions involving Pu may potentially be slow to reach local equilibrium in aqueous systems. These reactions may include two disproportionation reactions:

$$2Pu^{4+} + 2H_2O \leftrightarrow Pu^{3+} + PuO_2^+ + 4H^+ \qquad \text{(Eq. 16)}$$
$$\quad (IV) \qquad\qquad (III) \quad (V)$$
$$2PuO_2^+ + 4H^+ \leftrightarrow Pu^{4+} + PuO_2^{2+} + 2H_2O$$
$$\quad (V) \qquad\qquad (IV) \quad (VI) \qquad\qquad\qquad\qquad \text{(Eq. 17)}$$

And several electron transfer reactions including:

$$Pu^{4+} + PuO_2^+ \leftrightarrow Pu^{3+} + PuO_2^{2+}$$
$$(IV) \quad (V) \quad (III) \quad (VI) \qquad\qquad\qquad\qquad \text{(Eq. 18)}$$

And

$$PuO_2^+ + 4H^+ + e^- \leftrightarrow Pu^{4+} + 2H_2O \qquad\qquad \text{(Eq. 19)}$$

Equation 18 may be further divided into two half reactions:

$$PuO_2^{2+} + e^- \leftrightarrow PuO_2^+ \qquad\qquad\qquad\qquad\qquad \text{(Eq. 20)}$$
$$Pu^{4+} + e^- \leftrightarrow Pu^{3+} \qquad\qquad\qquad\qquad\qquad\quad \text{(Eq. 21)}$$

Notice for equations 16, 17 and 18 that Pu acts as both the oxidant and reductant within solution and so does not require the presence of additional oxidants or reductants for reactions to proceed. What is required, however, are substantial concentrations of the Pu product or reactant species identified by these reaction schemes. This means in systems (such as the environment) that maintain relatively low Pu concentrations, these reactions become less likely, while half reactions (requiring other oxidants or reductants) 19, 20, and 21 involving the transfer of a single electron become increasingly important [26]. Multi-electron transfer processes, while possible, are less likely than single electron transfer reactions and so are not listed [25]. An exception to this, discussed later, is the possible surface-mediated double electron transfer reaction between sorbed Pu(VI) and Pu(IV).

Inferences with regards to particular rates may be developed from reaction stoichiometry. Notice, reaction in equation 19 requires the making and breaking of oxygen bonds during electron transfer, while reactions in equations 20 and 21 do not. This additional requirement will significantly slow the rate of this reaction with respect to the rates of the others. This means the reaction in equation 19 will most likely limit electron transfer rates between reduced (Pu(III) and Pu(IV)) and oxidized (Pu(V) and Pu(VI)) Pu species in the environment.

A number of researchers have demonstrated the catalytic effect of adsorption on the kinetics of redox reactions for various metals [9, 10]. This effect has not been directly documented for Pu, however, a number of indirect experimental observations suggest surface-mediated redox

mechanisms may be important. Sanchez [5] first suggested the sorption of multiple valence states of Pu on the Fe-bearing minerals to explain the observed rate-limited sorption behavior and a reduction of the average oxidation state of Pu over time. Dissolved Pu is also reduced, but at a much slower rate, in systems containing only dissolved Fe and no mineral. These observations suggest a surface-mediated redox mechanism likely controls the sorption of Pu to Fe-bearing minerals.

Based on this information, a conceptual model for Pu has been developed. Here, all complexation, hydrolysis and sorption reactions between individual valence states of Pu are assumed to be at local equilibrium. In addition, single electron transfer reactions between Pu^{4+}/Pu^{3+} and $Pu^{V}O_2^{+}/Pu^{VI}O_2^{2+}$, which do not require the making or breaking of bonds, are assumed to be at local equilibrium. The only reaction described by a kinetic model is assumed to be the reversible surface-mediated reduction of sorbed Pu(VI) to sorbed Pu(IV). The rate equation for this reaction is shown in equation 22,

$$\frac{\partial Pu(VI)}{\partial t} = -k_f * \sum \left[\equiv SPu(VI) \right] + k_r * \sum \left[\equiv SPu(IV) \right]$$
(Eq. 22)

Where $\sum \left[\equiv SPu(VI) \right]$ represents the sum of the activities of sorbed Pu(VI) species, $\sum \left[\equiv SPu(IV) \right]$ represents the sum of the activities of sorbed Pu(IV) species, and k_f and k_r are the forward and reverse rate constants, respectively. These constants were derived from an experimental dataset previously published by Lu et al. [7].

Three-Phase Reactive Transport Model

It is not a simple task to explicitly correct for the buildup of surface charge on mineral colloid surfaces. Such an undertaking would require rewriting the *PHREEQC* code to enable equilibrium calculations of a colloidal third phase completely separate from dissolved and solid phases. This major rewrite, however, can be avoided by inserting a simple correction term into the master species list within the equilibrium database of *PHREEQC* assuming that the same mineral present as a mobile colloid is also present as an immobile surface [19]. This assumption would be valid for a typical groundwater system containing mineral colloids where the source of these particles is most likely from erosion of the pore walls. The correction term used to account for the buildup of surface charge on the mineral colloid is calculated assuming the surface charge density on the mobile and immobile surfaces are equal.

The method used to correct formation constants that describe sorption to mineral colloids for the buildup of surface charge follows similar steps taken by Allison et al. [27] for solid phase corrections. Recall from equation 13 that the apparent equilibrium constant for a surface complex formation reaction is equal to the product of the intrinsic equilibrium constant and a correction term, which can be expressed in terms of a new variable (X) as follows:

$$\left(e^{\frac{-F*\psi}{R*T}} \right)^{\Delta Z} = (X)^{\Delta Z}$$
(Eq. 23)

By restating the correction term as a power of ΔZ, the term X becomes equivalent to that of the activity of product or reactant defined within the formation reaction and the power term, ΔZ, is equivalent to the stoichiometric coefficient of that particular product or reactant [27].

To illustrate how the electrostatic correction term is included for mineral colloid species, three different hypothetical surface complexation reactions are considered.

$$\equiv SOH + M^+ \Leftrightarrow \equiv SOM + H^+ \tag{Eq. 24}$$
$$\equiv SOH + M^{+2} \Leftrightarrow \equiv SOM^+ + H^+ \tag{Eq. 25}$$
$$\equiv SOH + M^{+3} \Leftrightarrow \equiv SOM^{+2} + H^+ \tag{Eq. 26}$$

The surface charge in the reaction depicted by equation 24 is unaltered as a result of the reaction progression, so no correction of the equilibrium constant is required. However, the progression of reactions depicted in equations 25 and 26 both increase the charge on the colloidal surface. The K_{app} for these reactions are related to their K_{int} by the following relationships.

$$K_{app} = K_{int} * [X] \tag{Eq. 27}$$
$$K_{app} = K_{int} * [X]^2 \tag{Eq. 28}$$

In order to make the electrostatic correction for both reactions defined here, a fictitious species, Cor, with an activity of {Cor} is inserted into the surface complex formation reactions of equations 25 and 26 as shown.

$$\equiv SOH + Cor + M^{+2} \Leftrightarrow \equiv SOMCor^+ + H^+ \tag{Eq. 29}$$
$$\equiv SOH + 2Cor + M^{+3} \Leftrightarrow \equiv SOMCor_2^{+2} + H^+ \tag{Eq. 30}$$

The formation constants for these reactions then become equal to:

$$K = \frac{\{S \equiv OMCor^+\}\{H^+\}}{\{S \equiv OH\}\{M^{+2}\}\{Cor\}} \tag{Eq. 31}$$

$$K = \frac{\{S \equiv OMCor_2^{+2}\}\{H^+\}}{\{S \equiv OH\}\{M^{+2}\}\{Cor\}^2} \tag{Eq. 32}$$

If {Cor} is set equal to unity, equations 31 and 31 are equivalent to the uncorrected value of K_{int}. However if {Cor} is set equal to $(e^{-(F*\Psi/RT)})^{-1}$, then Equations 31 and 32 become equal to value of their respective K_{app}'s [27].

The existing two-phase (i.e., dissolved and solid) capability of *PHREEQC* was expanded to include a third colloidal phase in the following manner. Under the "RATES" keyword within *PHREEQC*, the function EDL("psi", "surface") returns the surface potential for an immobile "surface" in Volts. This function was used to call the surface potential of a particular immobile mineral surface present within a mixing cell. The value of the surface potential for the immobile surface was then be used within a user-defined kinetic rate equation to calculate the {X} term in
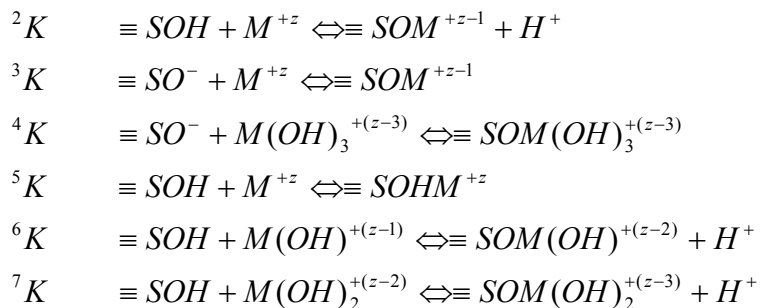
equation 23 and {Cor} terms in equations 31 and 32 in order to correct formation reactions of identical colloidal material defined within the dissolved phase of the *PHREEQC* model for electrostatic interactions. This method has been thoroughly validated against speciation generated from the built-in DLM for immobile surfaces provided in *PHREEQC* [19].

Table I   Binding constants for M(III) – M(VI) and kinetic constants for Pu on selected mineral surfaces derived using *INVRS-K*.

BINDING CONSTANTS								
Solid[1]	$[M_T]$ (M)	Element	I (M)	Log P_{CO_2} (atm)	Log K	# of Points	RSE (%)[8]	Data Ref.
Quartz	2e-9	Am(III)	0.005	-3.5	-0.18[2]	11	2.4	28
Quartz	1e-9	Eu(III)	0.05	-3.5	-1.66[2]	12	11	29
Alumina	5e-10	Am(III)	0.1	-3.5	3.2[2]	10	4.9	30
Montmorillonite (Si/Al = 1.2)	2e-9	Am(III)	0.005	-3.5	>8[2]	11	0.26	28
Montmorillonite (Si/Al = 1.2)	1e-9	Eu(III)	0.05	-3.5	12[2]	10	1.2	29
Biotite (Si/Al = 3)	2e-9	Am(III)	0.05	-3.5	1.36[2]	3	-	28,31
TiO$_2$	2e-8	Pm(III)	0.01	None	2.28[2]	8	1.7	32
Goethite	2e-8	Pm(III)	0.01	None	3[2]	6	1.7	32
Hematite	8e-14	Th(IV)	0.1	None	13.5[2]	15	9.7	33
Alumina	8e-14	Th(IV)	0.1	None	16[2]	9	9.6	32
TiO$_2$	3e-8	Th(IV)	0.04-0.005	None	10.2[2]	9	9.4	32
Goethite	1e-11	Pu(IV)	0.1	None	11.6[3], 23.5[4]	13	4.2	33,5
Hematite	1e-6	Np(V)	0.1	None	4.38[5]	15	5.1	34,35,36
Magnetite	1e-6	Np(V)	0.1	None	-2.05[6]	21	3.7	34
TiO$_2$	3e-5	Np(V)	0.01	None	-0.17[6]	5	7.3	32
Goethite	1e-10	Pu(VI)	0.1	None	1.06[6]	11	1.8	33
γ-Alumina	1e-10	Pu(VI)	0.1	None	-2.48[7]	6	1.7	32
Alumina	3e-10 - 3e-8	U(VI)	0.1	None	7.5[6]	22	2.4	31
KINETIC CONSTANTS								
Reaction				Log k_f	Log k_r	# of Points	RSE (%)[8]	Data Ref.
$\equiv SPu(VI) \Longleftrightarrow \equiv SPu(IV)$				-9.97	-11.8	6	7	7

[1]   Silico-aluminates were modeled assuming a stoichiometric ratio of Si and Al surface sites, employing silica and alumina acidity constants to represent protonation and deprotonation at these surfaces, and assuming only Al surfaces participated in the sorption of the metal.

[2-7] The formation constant is defined for the following reaction:

$$^2K \qquad \equiv SOH + M^{+z} \Leftrightarrow \equiv SOM^{+z-1} + H^+$$

$$^3K \qquad \equiv SO^- + M^{+z} \Leftrightarrow \equiv SOM^{+z-1}$$

$$^4K \qquad \equiv SO^- + M(OH)_3^{+(z-3)} \Leftrightarrow \equiv SOM(OH)_3^{+(z-3)}$$

$$^5K \qquad \equiv SOH + M^{+z} \Leftrightarrow \equiv SOHM^{+z}$$

$$^6K \qquad \equiv SOH + M(OH)^{+(z-1)} \Leftrightarrow \equiv SOM(OH)^{+(z-2)} + H^+$$

$$^7K \qquad \equiv SOH + M(OH)_2^{+(z-2)} \Leftrightarrow \equiv SOM(OH)_2^{+(z-3)} + H^+$$

[8] Relative Standard Error (%).

RESULTS

A summary of regression results from this research is shown in Table 1. A total of 18 regressions were conducted on sorption data from chemical analogs of Pu and, in a few well-defined cases, systems containing Pu. The relative standard errors of all model fits to experimental data were less than 10% and typically below 5%. In all cases for the analogs, the introduction of a single new surface species allowed adequate simulations of the observed behavior over a range of pH values.

Binding Constants for Pu from redox Stable Analogs

Theory alone is not capable of deriving binding constants due to the complicated influences of both ion size and charge [16]. However, these constants may be developed for the individual oxidation states of Pu on mineral oxide surfaces if first hydrolysis and binding constants of their chemical analogs are known. Implicit within every hydrolysis constant is information on the size and charge of that individual ion. Dugger et al. [37] were the first to show a linear relationship between binding strength and the first hydrolysis constant for various divalent metals. Wang et al. [17] showed a similar, but less definitive, relationship between the first hydrolysis constants and binding strength to a variety of mineral surfaces for actinides. Binding constants regressed upon here for the reaction presented in equation 25 provides an improved linear relationship to that presented by Wang et al. and are shown in Fig. 1. The linear function derived from the data is:

$$LogK_{Sorption} = 2.32x(LogK_{MOH}) + 17.5 \quad (R^2 = 0.91) \tag{Eq. 33}$$

Equation 33 provides a tool for predicting the adsorption for cations for which aqueous speciation has been characterized but only limited or no sorption data exist. The 95% confidence interval for the Log $K_{sorption}$ about the trend line is $\pm$ 0.8 log units, indicating that binding strength for each of the cations does not vary greatly for different types of minerals surfaces. Rather a more important factor controlling Pu sorption behavior to mineral oxide surfaces seems to be at what pH range, in relation to Pu dissolved speciation, are oxide surfaces protonated and deprotonated [23]. Using equation 33, the log of the sorption constants for Pu^{+3}, Pu^{+4}, $Pu^VO_2^+$, and $Pu^{VI}O_2^{+2}$ onto a generic mineral oxide surface were calculated to be 1.5, 15.7, -5.0, and 4.7, respectively.

Other Sorbing Species of Importance

The binding constants derived from Fig. 1 may not represent all of the important Pu dissolved species that sorb to a mineral surface. The binding constants for Pu^{3+} and PuO_2^+ species likely represent Pu(III) and Pu(V) sorption behavior adequately. This is assumed so since these dissolved species each make up a majority of the dissolved phase of their respective valence state and maintain a higher positive charge than other potentially important dissolved species. This assumption is likely not valid for Pu(IV) and Pu(VI). While it is expected that Pu^{4+} and PuO_2^{2+} likely represent the strongest binding species (based on effective charge) for their respective oxidation states, the concentration of these species may be orders of magnitude lower than some tetravalent hydrolyzed species and hexavalent carbonato species. As a result, binding constants may also be required for these species.
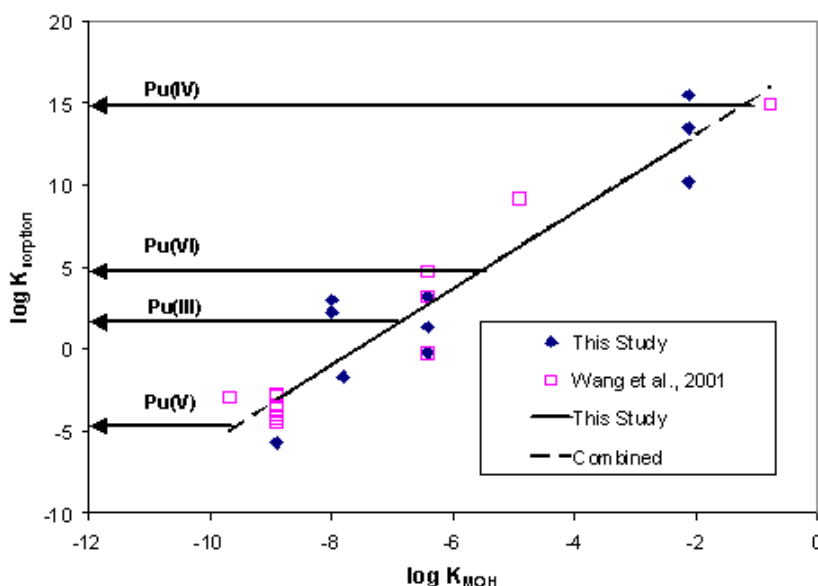
Fig 1 Order of binding strength onto mineral surfaces for the four oxidation states of Pu.

It is possible to derive Pu(IV) sorption constants directly from data measured from carefully controlled experimental systems. This is possible since nearly pure Pu(IV) solutions may be prepared in the laboratory and the binding strength for the other competing oxidation states are small in comparison to that of dissolved Pu(IV) species. This means, it can be safely assumed that all sorbed Pu within these experimental systems exist in the tetravalent oxidation state. Results from a regression conducted here on such a system is presented in Table 1 and confirms that the sorption onto minerals by other (likely hydrolyzed) Pu(IV) species must be considered. Pu(VI)-carbonato species may represent a significant fraction and greatly influence the overall sorption behavior of dissolved Pu(VI) at higher environmental pH ranges. Unlike Pu(IV), it may not be possible to directly measure binding constants for Pu(VI) since these solutions are quickly reduced in the presence of Fe-bearing minerals. Fortunately, binding constants derived for U(VI) on minerals at high pH are available [38]. Based upon the similarity in first hydrolysis constants for hexavalent U($\log K_{OH}$ = -5.1) and Pu($\log K_{OH}$ = -5.5), it was assumed that U(VI)-

carbonato binding constants provided an adequate value for those expected for Pu(VI) without ion size and charge corrections.

Estimation of Kinetic Constants

Painter et al. [11] derived their forward "slow" rate constant, α (see Eq. 1 and 3), for the kinetic sorption model from experimental data reported by Lu et al. [7] by assuming β roughly approximated zero over the experiment duration. For comparison purposes, values for the forward and reverse rate constants for equation 22 were regressed upon using *INVRS-K* and the same experimental data used by Painter et al.. Best-fit estimates for these values are reported in Table 1. Figure 2 compares model fits by the phenomenological and mechanistic approaches to the experimental data. The mechanistic model seems to simulate observed Pu sorption kinetics better than that of Painter et al.'s model. This was attributed to slight differences in the conceptual design of the two model approaches, with the mechanistic model approach more closely approximating reality.
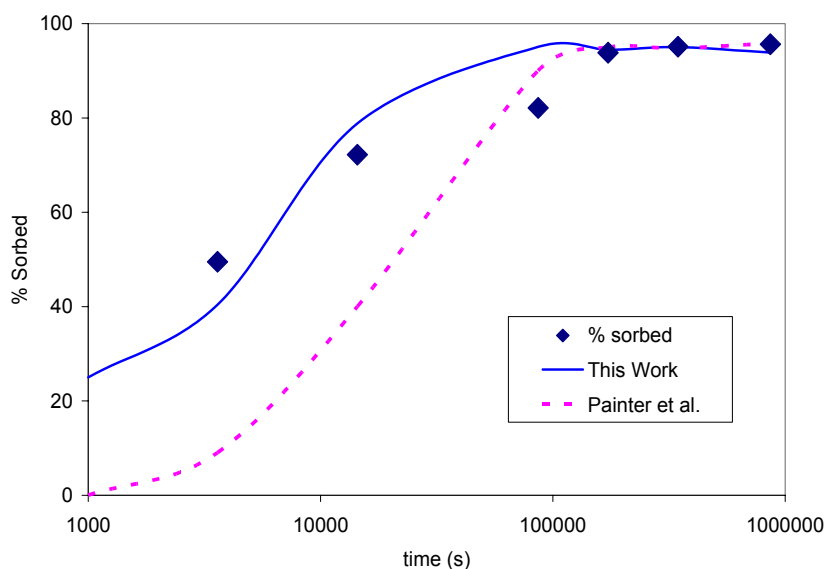

Fig 2. Mechanistic (solid line) and phenomenological [11] (dashed line) kinetic model fits to experimental data from [7] of Pu sorbing to Fe-bearing minerals over time. System characteristics: pH = 8.4, [Pu] = 2.68E-7 M, Alkalinity = 25 meq L^{-1}, 0.2 gL^{-1} hematite having surface area = 53.5 m^2g^{-1}.

DISCUSSION

Testing Simplifying Assumptions of Previous Models

One purpose for these modeling exercises is to understand experimental requirements for deriving model parameters and minimizing prediction uncertainty. By assuming the "slow" reverse rate constant (β) was zero over the time frame of the sorption experiment, Painter et al.

[11] was able to derive an equation that related experiment duration required for obtaining the detection limit for α as,

$$\alpha_0 = \frac{1}{t_E} \ln(1.01) R_C \qquad \text{(Eq. 34)}$$

Where t_E is the required experiment duration and $R_C = 1 + Y$ (see Eq. 2). They concluded based on this equation that adequate measurements of rate constants for sorption onto some minerals might require unrealistically long experiments. As an example adequate measurement of a $\alpha = 2.9\text{E-}6$ h^{-1}, which was found to enhance migration by ~100, is measurable only after 300 days of experiment time [11]. However, the validity of equation 34 is based upon the assumptions that the kinetic model correctly represents actual mechanisms and that the reverse rate of this mechanism is zero over the entire duration of the experiment. These assumptions are investigated by comparison with the mechanistic modeling approach.

There exist several important differences between the phenomenological and mechanistic kinetic models. While the phenomenological approach treats "fast" and "slow" sorption sites on colloids independently, these processes are likely not independent of one another. In fact, the source of sorption rate-limitations for Pu is most likely due to transitions between Pu on Painter et al.'s "fast" and "slow" sites, not by the process of sorption itself (which should be much faster). The Pu on the "fast" and "slow" sites in the phenomenological model roughly represents sorbed Pu(VI) and sorbed Pu(IV), respectively. The mechanistic approach assumes sorption of these species adequately approaches equilibrium, while the reaction between these species is considered rate-limited. The assumption that these mechanisms are not independent is supported by the superior model fit (see Fig. 2) to the experimental data (standard error = <7%) compared to that of the phenomenological approach (standard error = 30%). Notably, the mechanistic model is further constrained by the assumption of reversibility and the fact that 1st order reaction rates are based upon theoretical estimates of local equilibrium between the Pu(IV) and Pu(VI) dissolved and sorbed species. Also notable, mechanistic model fits to the experimental data could not be achieved by assuming β equals zero, which calls to question the validity of equation 34. While a rigorous analysis of mechanistic model parameters was not conducted here, any rate limitations were not noticed in the experimental results past a few days time. The reverse rate constant is about two orders of magnitude lower than the forward rate constant, so precise estimations of this constant may be more tedious. In any case, these results illustrate that while the initial development of mechanistic models may be more time consuming than simpler phenomenological models, estimating the model parameters may not be.

Sorption Kinetics and Colloid-Enhanced Migration

The most significant issue with the phenomenological model developed by Painter et al. [11] is the time dependent sorption asymmetry between colloid and immobile solid phases. At time zero the model assumes that Pu symmetrically sorbs to both colloid and immobile solid phases. After time zero, however, this symmetry is lost due to the growing "slow" colloidal sorption term. Since there are no "slow" immobile solid phase surfaces defined in Painter et al.'s model, colloids out-compete immobile phases for Pu over time regardless of the number of colloid binding sites available relative to those of the immobile solid phase. Phenomenological model

predictions of the kinetic-limited, colloid-enhanced, migration of Pu is presented in Fig. 3 for comparison purposes [11]. The time-dependent symmetry of the model manifests itself as an increase in the predicted relative Pu discharge with time. This may well represent a potentially real sorption mechanism (e.g., the "Onion Effect"). However, a more likely scenario would be that kinetic limitations exist for Pu sorption to both colloids and immobile solid phases. Predictions for the same system generated using the mechanistic model are also presented in Fig. 3, identified as "This Work – Dissolved."   These predictions show that sorption kinetics enhances migration of Pu when introduced as an oxic (Pu(V) or Pu(VI)) dissolved species. However while Painter et al.'s model predicts a relative enhancement of roughly 10^6 over that of the "no colloid" case, mechanistic model predictions estimate migration is enhanced by only a factor of 3. The discrepancy between the models was attributed to a bias towards pseudo-colloid formation in the kinetic equation of the phenomenological model.

To fully realize the importance of kinetics on Pu colloid-enhanced migration, a simulation was also conducted assuming Pu was initially in the form of Pu(IV) pseudo-colloid. This simulation roughly represents groundwater migration of Pu originating from a surface water source where immobile surfaces are absent and colloids are the only significant sorbing surface. Results of this simulation are shown in Fig. 3, identified as "This Work – Pseudo-colloid." These results indicate the form and manner in which Pu is introduced to a system may greatly affect its overall mobility in groundwater.
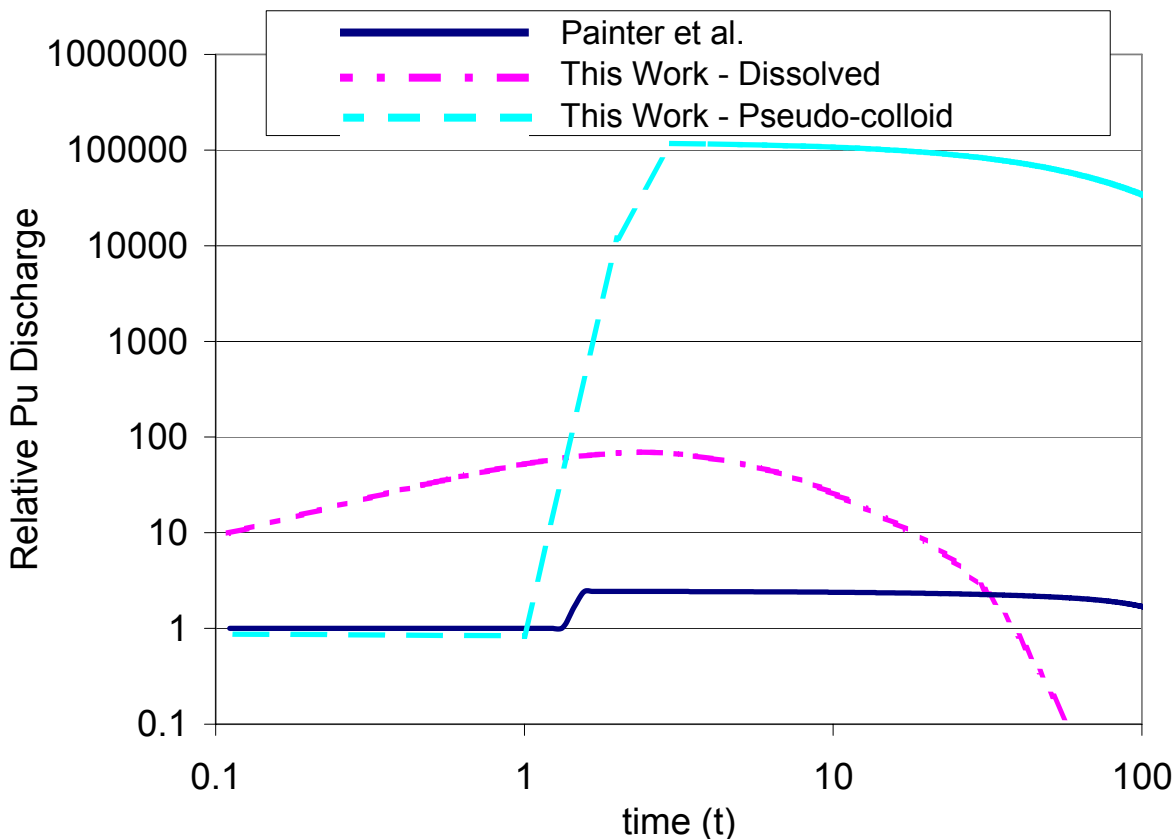
Fig. 3 Comparison of mechanistic and phenomenological model predictions
of sorption kinetic effects on colloid-enhanced migration of Pu for the
alluvial aquifer near Yucca Mountain, Nevada. Pu discharge is plotted
relative to the "no colloid" case. Time (τ) is relative to the mean
residence time of the aquifer (4000 yrs). Important model parameters:
Painter et al. [11] - K_d=5 L/g, $\alpha = 100$, $\beta = 0$, $\theta = 0.3$, and $\rho = 2400$
kg/m^3; Mechanistic model – pH = 8.2, mobile to immobile binding site
concentration ratio $\cong$ 1E-2, all other parameters identical to those listed
in Fig. 2. Model results from this work were generated assuming Pu
was introduced to the system as either a oxic (V/VI) "Dissolved"
species or a reduced (IV) "Pseudo-colloid" species.

Other Environmental Factors

Environmental factors other than sorption kinetics may affect Pu migration and are important
considerations when developing engineered barriers and assessing future potential risk of a
contaminant. Factors including colloid to immobile solid phase binding site concentration ratio,
pH, and carbonate concentration were modeled to illustrate their potential influence on Pu
migration. Simulations were conducted on systems identical to that shown in Fig. 3 with the

exception of changes for each of the environmental factor considered. Results of these simulations are presented in Fig. 4.
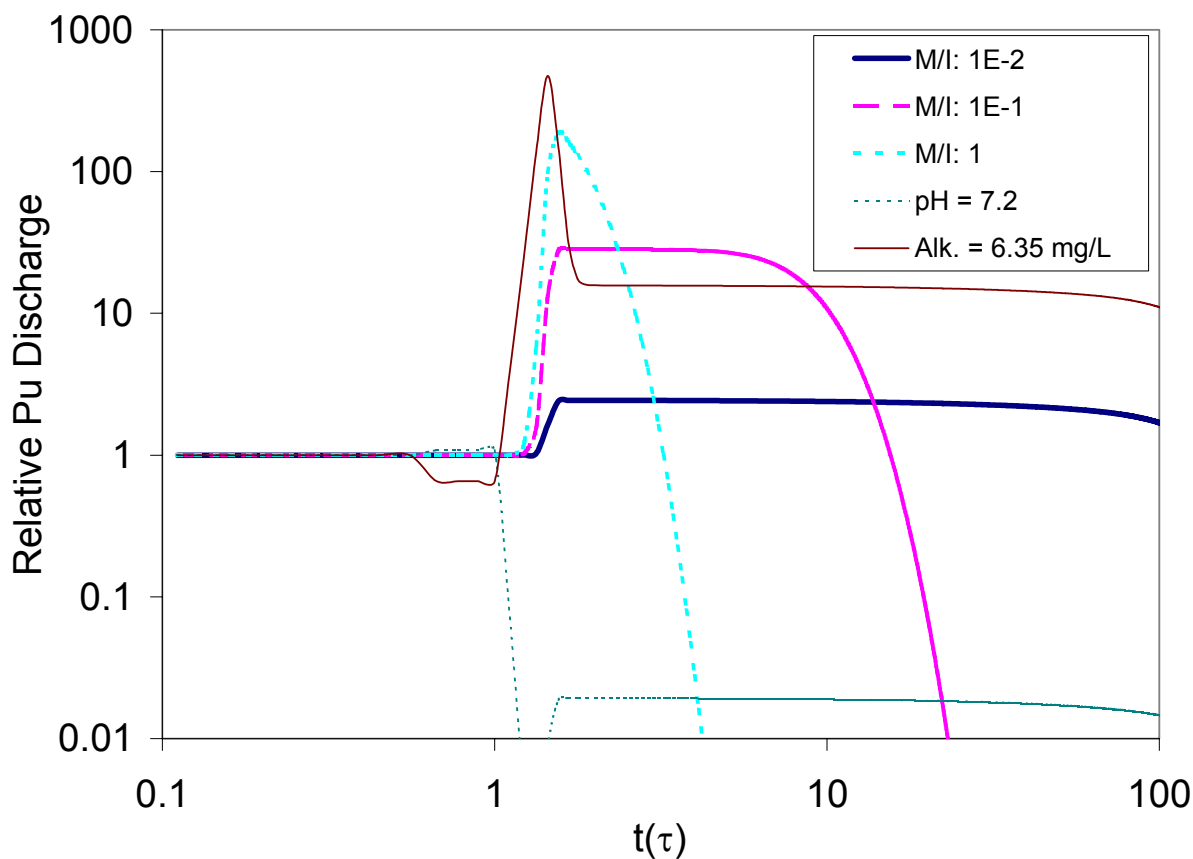

Fig. 4. Potential environmental influences on Pu migration in the aquifer near Yucca Mountain. Model parameters are identical to those listed in Fig.'s 2 and 3 unless otherwise specified. M/I = mobile to immobile binding site concentration ratio.

Colloid-enhanced migration of Pu markedly increases as the ratio of mobile to immobile binding sites approaches unity (Fig. 4). This rather obvious conclusion illustrates the need for precise field measurements for these model parameters. However, such predictions could have been made using a simpler phenomenological model. A capability unique to the mechanistic model is the ability to predict effects due to changing chemistry.

Figure 4 also presents predictions when the system pH is decreased by 1 unit and the alkalinity is decreased by a factor of four. Both effects significantly alter the original prediction results in a way that may not have been easily predicted without a model. A slight drop in pH likely causes desorption of Pu to occur. However, it also causes a shift in the redox distribution to favor more reduced species. Since sorbed Pu is mostly in the form of reduced Pu(IV) and immobile solid phase binding sites outnumber colloid binding sites, the overall effect of this pH change on migration is negative. Decreasing carbonate by a factor of four caused an increase in the

predicted migration likely due to a shift from oxidized PuO_2-carbonato complexes to pseudo colloidal species.

CONCLUSIONS

Predictions of colloid-enhanced migration of Pu generated from a newly developed mechanistic model are compared with those from a simpler model using a phenomenological approach. This comparison identified several shortcomings of approaches that implicitly combine numerous chemical mechanisms within one or a few model parameters. These shortcomings include a kinetic sorption model that produces time-dependent asymmetric sorption mechanisms between the colloid and immobile solid phases. This progressively favors pseudo-colloid production over that of immobile solid phase retardation and over-predicts the effect sorption kinetics have on Pu migration.

Model simulations were also carried out using the mechanistic model to illustrate how changes in the initial source of Pu, pH, carbonate concentration, and the mobile to immobile binding site ratio might alter the overall migration behavior of Pu. These influences, most of which can only be predicted using a mechanistic model, may greatly affect contaminant mobility in the groundwater and illustrates the need for employing this approach when predicting behavior of chemically complex contaminants like Pu.

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