



U.S. DEPARTMENT OF
ENERGY

PNNL-18434

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Utility of Mechanistic Models for Directing Advanced-Separations Research-and-Development Activities:

Electrochemically Modulated Separation Example

JM Schwantes

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Pacific Northwest
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Summary

Executive Summary

The objective for the work herein described was to demonstrate the utility of mechanistic computer models designed to simulate actinide behavior for use in efficiently and effectively directing advanced laboratory R&D activities associated with developing advanced separations methods.

This report summarizes the development and results generated from a mechanistic model designed to simulate EMS of actinide elements, an advanced on-line separation method currently under development at Pacific Northwest National Laboratory. These model simulations compared well with experimental observations, suggesting the major chemical species and reactions controlling behavior within the system were adequately represented in the model. In addition, the model was used to simulate conditions for EMS not yet tested in the laboratory that might be suitable for pre-separation of neptunium. Despite the fact that relatively inaccurate, estimated, values for surface complexation constants were used here, these simulations illustrate the utility of mechanistic models for directing R&D activities related to advanced separations methods for the actinides. Future work needs to be done to develop more accurate constants and models for accurately simulating a wider variety of separations techniques.

Acronyms and Initialisms

CCM	Constant capacitance model
DLM	Diffuse layer model
DSA	Direct substitution approach
EMS	Electrochemically Modulated Separation
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
PDEs	Partial differential equations
SCMs	Surface complexation models
SIA	Sequential iteration approach
TLM	Triple layer model

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1.0 Overview/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 reality. Adequate predictions, however, are possible if the behavior-controlling mechanisms within the system are identified and accurately represented.

Models designed for chemical systems fall into one of two general classes: empirical and mechanistic. As the name suggests, empirical models do not attempt to simulate individual reactions and species, but rather the combined effects these reactions and species exhibit as a function of major variables (e.g., pH, temperature, analyte concentration, etc.). Empirical models of a particular system are typically generated by fitting curves to experimentally observed behavior of that system as a function of changing system parameters of interest. While these types of models are adept at representing complex systems, they are limited in application to the specific system and set of conditions from which the models were derived. This limits the usefulness of applying empirical models to theoretical systems that have yet to be generated and studied in the laboratory.

Mechanistic chemical models, unlike empirical models, attempt to simulate overall behavior by explicitly accounting for all major reactions and chemical species within a system. By doing so, mechanistic models have the advantage over empirical modeling approaches of being able to predict behavior under conditions outside those used to develop the model constants. This, of course, assumes all important reactions and species within the system being modeled are accurately represented by the model. When this assumption is met, such a model then becomes a tool for “virtual” investigations under a wide range of conditions – *minimizing labor, instrument, and waste disposal costs associated with laboratory investigations.*

For several reasons, the widespread application of chemical prediction tools for guiding laboratory investigations has not occurred. In some cases, important thermodynamic constants are either missing from the database or are not accurate enough to predict behavior adequately. In other cases, important reacting species in complex systems may never reach equilibrium and therefore may require kinetic models for accurate predictions. Or possibly, systems of interest may be associated with high ionic strength outside the bounds of accurate predictions by currently-available mechanistic chemical models. Certainly, these models are in their infancy with regards to simulating rate-limited reactions and behavior in high ionic-strength media. However, there is utility in developing capable simulations of simple systems at equilibrium or even applying these simple equilibrium models to kinetically controlled systems as a means of qualitatively assessing the extent kinetics play in the overall behavior of a species within such a system. In addition, these models will find even broader application as enhancements are made to accurately deal with kinetics and high ionic-strength media.

In this report, we record the development and use of a mechanistic model for simulating actinide behavior during Electrochemically Modulated Separation (EMS). EMS is a new on-line method [Schwantes In Press] used for separating uranium and plutonium from complex matrices and each other prior to their quantification by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The EMS apparatus is relatively simple, comprised of a glassy carbon electrode within a flow-through cell. By controlling the applied potential, uranium or plutonium will either accumulate or release from the electrode surface in 2% HNO₃ solutions. As a result, the system has been used to preferentially accumulate one or the other of the

actinides away from complex matrices under the accumulating potential, and then release the element into a clean solution for analysis by ICP-MS. The exact chemical mechanisms that allow this separation are unknown, although either precipitation or sorption processes are hypothesized as being important. Here, we compare model and experimental results to illustrate how these models can provide some information about the mechanisms controlling behavior. We also attempt to use the model to simulate conditions outside those that have been investigated in the laboratory as a means for directing future experimental research.

2.0 Materials & Methods

2.1 Equilibrium Model Development

A chemical equilibrium model is a type of mechanistic model. While a wide variety of chemical equilibrium models have been developed [Parkhurst 1999; Wolery 1992; Bethke 1996], all take essentially the same approach to solving the set of coupled nonlinear differential equations that define the species and reactions within a system. These models define one master aqueous species associated with each element or element valence state, plus three more for the activities of the hydrogen ion, the aqueous electron and water. The mass action equation for an aqueous species “i” in terms of master species (m) is represented by Equation 1.

$$K_i = a_i \prod_m^{M_{aq}} a_m^{-c_{m,i}} \quad (1)$$

K_i is a temperature-dependent equilibrium constant, $c_{m,i}$ is a stoichiometric coefficient that is equal to the mole ratio of master species to species i in the equation that forms species i from only master species. It is negative if the species appears on the right-hand side of the formation reaction and positive if it appears on the left-hand side. M_{aq} is the total number of aqueous master species in the system. The activity for species i (a_i) is equal to the product of the activity coefficient and molality of the species. The activity coefficient for a species is calculated by the equilibrium model using (typically) either the Davies equation or the extended Deybe-Huckel equation. More discussion on these equations may be found in the literature [Bethke 1996; Langmuir 1997]. The total moles (n) of an aqueous species i in the system may be derived from the mass action equation and is equal to

$$n_i = K_i W_{aq} \frac{\prod_m^{M_{aq}} a_m^{c_{m,i}}}{\gamma_i} \quad (2)$$

where W_{aq} is the mass of the water in solution and γ_i is the activity coefficient of species i. The total moles of master species “m” in the system as aqueous species ($T_{m,aq}$) may be represented by the sum of the moles of the element in all aqueous species by

$$T_{m,aq} = \sum_i^{N_{aq}} c_{m,i} n_i \quad (3)$$

where N_{aq} is the total number of aqueous species. Similar summations are made for contributions from pure phases (p), solid solutions (ss), exchange species (e), surface species (s) and gas phases (g). These summations are subtracted from the total number of moles of master species m (T_m) present in the system in order to define the function f_m :

$$f_m = T_m - T_{m,aq} - T_{m,p} - T_{m,ss} - T_{m,e} - T_{m,s} - T_{m,g} \quad (4)$$

Once a set of functions, f_m , has been developed for the entire system, they can be solved simultaneously for the set of unknown activities of the master species. A solution to the set of nonlinear equations is found when all functions, f_m , equal zero.

The Newton-Raphson algorithm is a method for solving sets of non-linear equations. It involves iteratively revising an initial set of values for the unknowns until they are sufficiently close to the solution. A set of equations relating f_m to an estimate of the error (dx_j) for unknown j , may be represented by

$$f_m = -\sum_j^U \frac{\partial f_m}{\partial x_j} dx_j \quad (5)$$

where U is the total number of unknowns. This set of equations can be solved for the set of dx_j and new values of the unknowns, x_j^{l+1} , can be calculated by the equation

$$x_j^{l+1} = x_j^l + dx_j \quad (6)$$

where l is the iteration number. The process is repeated until the values of all functions are less than a specified tolerance.

2.2 Surface Complexation Models

Since sorption mechanisms may be responsible for controlling the behavior of actinides through the EMS system, it is necessary to develop a model capable of simulating the sorption process effectively. The need for more capable methods to simulate sorption behavior has led 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 actinides. A summary of the detailed descriptions of SCMs provided by Davis and Kent [1990] and Dzombak and Morel [1990] is provided here.

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



where $\equiv SOH$, $\equiv SOH_2^+$, and $\equiv SO^-$ represent possible neutral, positively charged and negatively charged species. Equations 7 and 8 may be defined by intrinsic (identified by *) equilibrium constants as

$$K_+^* = \frac{\{\equiv SOH_2^+\}}{\{\equiv SOH\}\{H^+\}_S}, \quad (9)$$

and

$$K_-^* = \frac{\{\equiv SO^-\}\{H^+\}_S}{\{\equiv SOH\}}; \quad (10)$$

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 and 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. 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.

$$\{X^{+Z}\}_S = \{X^{+Z}\} \left[e^{-\psi F / RT} \right]^Z \quad (11)$$

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 11 to relate the intrinsic equilibrium constant in terms of ion activity in the bulk solution. For the reaction represented by Equations 7 and 8, the expression in terms of bulk hydrogen ion activity becomes

$$K_+^* = \frac{\{\equiv SOH_2^+\}}{\{\equiv SOH\}\{H^+\} \left[e^{-\psi F / RT} \right]^Z} \quad (12)$$

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}O₂⁺² by the reaction



is considered. The intrinsic equilibrium constant describing this reaction is

$$K^* = \frac{\{\equiv SOPuO_2^+\}\{H^+\}_S}{\{\equiv SOH\}\{PuO_2^{2+}\}_S} = \frac{\{\equiv SOPuO_2^+\}\{H^+\} \left[e^{-\psi F / RT} \right]}{\{\equiv SOH\}\{PuO_2^{2+}\} \left[e^{-\psi F / RT} \right]^2} = \frac{\{\equiv SOPuO_2^+\}\{H^+\}}{\{\equiv SOH\}\{PuO_2^{2+}\} \left[e^{-\psi F / RT} \right]} \quad (14)$$

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.

$$K^* = K^{APP} \left[e^{-\psi F / RT} \right]^{-\Delta z} \quad (15)$$

For model simulations of surface complexation onto glassy carbon, we assume only the $\equiv SOH$ surface functional group participates in sorption. This assumption, under the current study, is adequate since pH is not adjusted during the EMS operations simulated.

Several of the most popular SCMs are the two-layer diffuse layer model (DLM), 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 [Xu 1999]. A DLM is used in our work and was chosen for its simplicity and comparison with a larger number of previously published works.

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 dependent 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. For the development of the models used here, best available formation constants were taken from the literature for each of the elements modeled in this research. The *WATEQ4F* [Ball 1991] thermodynamic database was augmented with best available constants for the actinides as suggested by several extensive reviews [Cross 1991; Schwantes 2002; Lemire 2001; Lemire 2003; Morss 2006]. Due to the unusual reduction potentials reached during EMS, thermodynamic constants for a few key uranium and neptunium species were not available. In those cases, estimates for their values were used based upon known constants of similar actinides. In addition, no sorption constants have been generated for actinides on glassy carbon surfaces. However, the relative binding strength of actinides to surfaces is well known [Schwantes 2004; Wang 2001]. This basic knowledge was used to generate relative values for constants describing actinide sorption to glassy carbon. These relative values were then adjusted in parallel to fit experimental observations. A single binding site type with a constant site density equal to 2.3×10^{18} sites m^{-2} was assumed for the glassy carbon surface of the EMS system, consistent with recommendations by Dzombak and Morel [1990] for mineral oxide surfaces. Ionic strength corrections were made using the relatively simple Davies equation [Parkhurst 1999]. 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 relatively low (~ 0.1 M) ionic strength.

2.3 Reactive Transport Model

A reactive transport model, which combines an equilibrium or kinetic model with a flow module in order to calculate spatio-temporal variations in concentrations of chemicals, was needed in order to simulate the flow-through EMS system. For a reactive transport model, sets of partial differential equations (PDEs) are written to represent the simultaneous evolution of chemistry and solution flow. Two general approaches to solving these PDEs have been taken [Xu 1999]. One tactic solves chemical and transport equations simultaneously, while the other solves them separately. The direct substitution approach (DSA) simultaneously solves the coupled problem by directly substituting chemical equations into the transport equations. This method produces a system of highly non-linear transport equations that may not be well conditioned in multi-dimensional models. Another mathematical technique is known as the sequential iteration approach (SIA). SIA solves transport and chemical equations separately and sequentially converges on an answer, if need be, in an iterative fashion. Several performance issues arise from the differences in the two general approaches. First, chemistry is inherently dependent upon transport processes and, as such, cannot be separated from them without introducing a certain amount of numerical error. Because of this fact, DSA is inherently a more accurate representation of reality than the SIA approach. However, another issue is that due to the highly non-linear nature of equations formed by the

DSA, it requires more computer time and memory than the SIA, and DSA may also become unstable when applied to multi-dimensional problems. As a result, the SIA is usually the approach of choice for more complex two- and three-dimensional models. That said, numerous examples exist in the literature in which both DSA [Valocchi 1981; Jennings 1982; Miller 1983] and SIA [Kirkner 1984; Walsh 1984; Cederberg 1985] have been utilized effectively within reactive transport models.

A set of PDEs must be solved regardless of whether chemical and transport equations are solved separately or simultaneously. Depending upon the required capability of the model being designed, either a finite-difference or a finite-element approach is used to solve these PDEs. A finite-difference approach divides the solution domain into a grid of discrete points. A PDE is written for each of these points and its derivatives are replaced by finite divided differences. A finite-difference approach, such as the Crank-Nicholson approach, is efficient and well-suited for one-dimensional systems that may be approximated with uniform grids [Chapra 1998]. Finite difference methods have been developed for multidimensional systems, but are usually unstable and become less efficient than finite-element approaches at dimensions greater than one [Chapra 1998]. A finite element approach divides the solution domain into a series of shapes or elements instead of discrete points. The total solution is calculated in a piecewise fashion with all of the elements in the domain, taking care to satisfy conditions at the inter-element boundaries. A finite-element approach is more complicated to apply and requires greater computational resources for one-dimensional problems than a finite-difference approach, but excels for systems of complex geometry. Where characteristics in several dimensions are important, two- and three-dimensional reactive transport models are employed. These models are designed to handle systems of complex geometry and usually require a finite element approach.

2.4 Special Case: One-dimensional “Mixing Cell”

Several popular one-dimensional reactive transport models such as PHREEQC [Parkhurst 1999] and EQ3/6 [Wolery 1992] simulate flow using a finite-difference approach. These models utilize a series of “mixing cells” in which chemical reactions are calculated [Brown 1998]. Before the transport step, equilibrium is calculated within each mixing cell. The contents of each cell are then shifted to the adjacent downstream cell, where the solutions are equilibrated once again. The mixing-cell approach is similar to SIA in that chemical and transport equations are kept separate during calculations. However, unlike the SIA approach, in which if results do not fall within specified tolerances equations are refined and recalculated iteratively, the mixing-cell approach stops at calculating equilibrium before and after a transport step. Consequently, the amount of computational effort required by the mixing-cell approach is significantly reduced compared with that of the SIA. A tradeoff, however, is that the mixing-cell approach may be subject to greater numerical error than the SIA. Several comparisons of mixing cells with the SIA show good agreement between the two approaches, indicating that the numerical error introduced by using a mixing-cell approach over an SIA approach is minimal [Glynn 1991; Brown 1998].

2.5 Electrochemically Modulated Separation

The EMS system consists of a small flow-through cell containing a glassy carbon electrode (Figure 1). By applying a range of potentials across the working electrode, the EMS is able to individually accumulate actinides onto, or release from, the electrode surface, providing an on-line means for separating these elements from complex matrices or from each other. To date, EMS has been applied successfully as an

on-line means for pre-separating both plutonium and uranium prior to their analysis via ICP-MS. Studies are underway to apply EMS to other actinide elements and couple this technology to non-destructive assay methods like gamma spectrometry.

The In-Line Electrochemical Flow Cell Schematic in Cross-Section

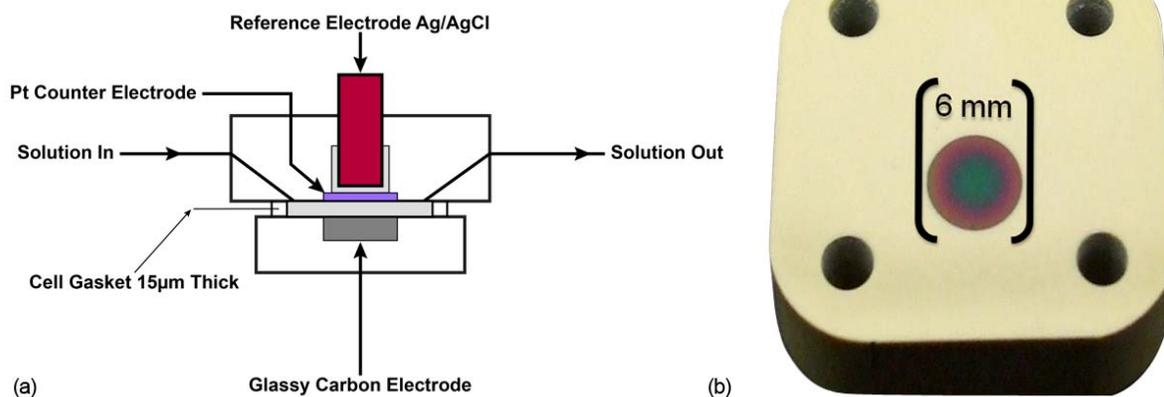


Figure 1. (a) Schematic of the EMS flow cell and (b) picture of the anodized glassy carbon working electrode

Model simulations of the EMS system shown in Figure 1 were conducted using an equilibrium model coupled to a 1-D mixing cell. Chemical reactions were assumed to reach an equilibrium state as defined by the thermodynamic database used. Typically, this assumption would not be accurate for chemical reactions involving redox transformations of actinide species across the free (An(III, IV) / An(V, VI) boundary [Choppin 1983]. However, experimental data from the EMS suggest at the typical operating flow rates, these reactions are adequately represented with an equilibrium model. A total of 10 mixing cells 150 μm in length were used to simulate the electrode surface within the flow cell of the EMS system. Dispersivity in all of the mixing cells was assumed to be equal to 0.002 meters and diffusion coefficients were set to zero.

3.0 Results & Discussion

3.1 Important Actinide Species and Reactions

Sources for accurate thermodynamic constants describing a number of reactions and species of plutonium under conditions expected during EMS are available from the literature [Baes 1976; Cross 1991; Schwantes 2002; Lemire 2001; Lemire 2003; Morss 2006]. This is not necessarily the case, however, for more redox stable actinides that are harder to study under extreme reduction potentials. As a result, we modeled the distribution of plutonium dissolved species in order to identify the species dominating behavior under variable redox conditions. Figure 2 shows results of those simulations. Table 1 lists the dissolved species that were found to dominate behavior of plutonium under redox conditions expected during EMS.

Due to the extreme redox conditions generated during EMS, a few important reactions and species of uranium and neptunium under these conditions that have not been well described in the literature based upon model simulations of dissolved plutonium species (see Table 1). In these few cases, it was important to estimate values for missing constants based upon values of other actinide analogs. Those estimated values are provided in Table 1.

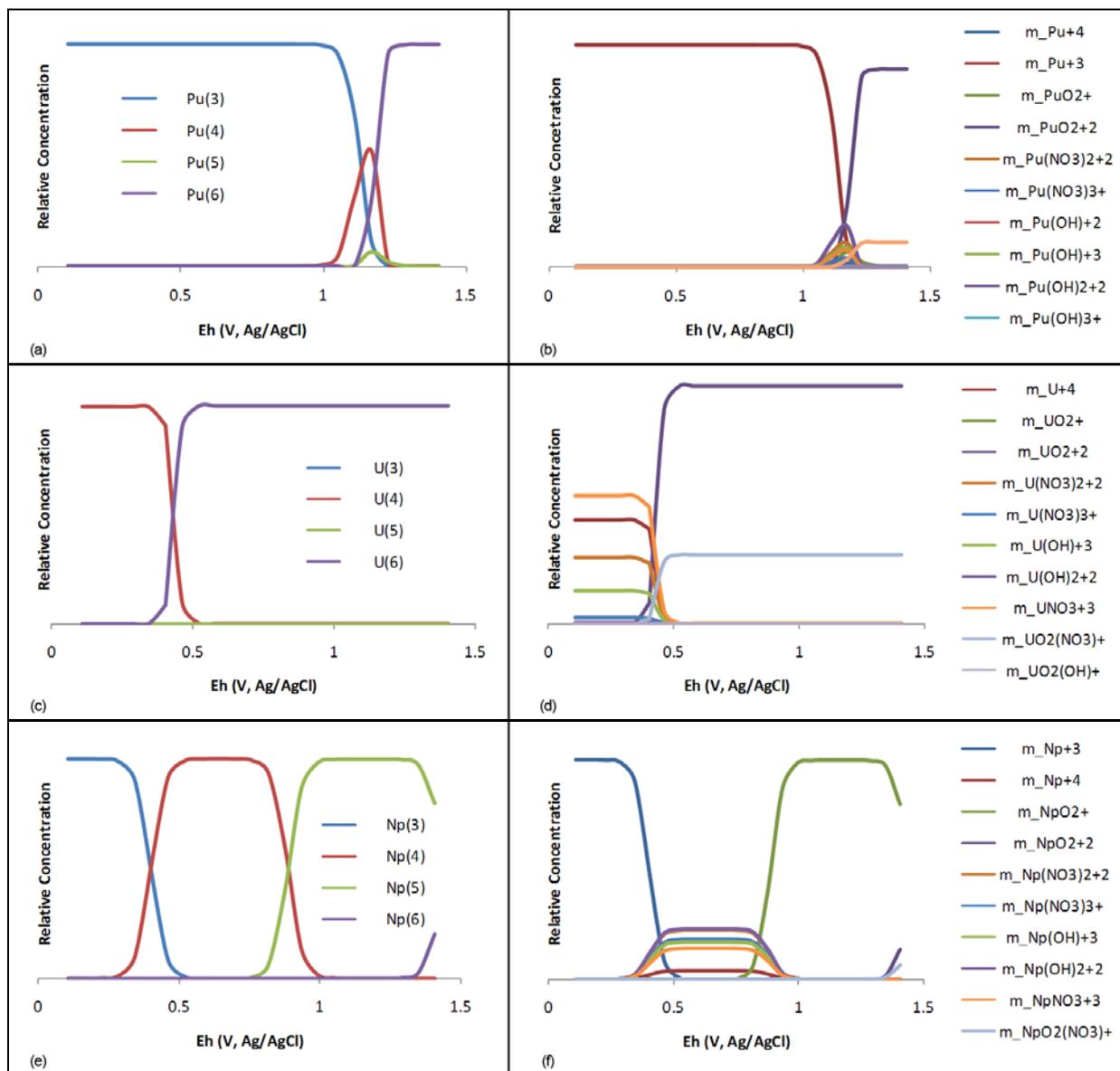


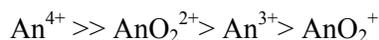
Figure 2. Plutonium speciation in 0.1 M HNO₃ under variable reduction potentials

Table 1. Thermodynamic constants for reactions and species thought to control actinide behavior during EMS (from Lemire et al., [2001; 2003] unless otherwise noted)

Reaction	Pu	U	Np
An(III)			
$An^{+3} + e^- \leftrightarrow An^{+2}$	17.69	-8.796	9.995
$An^{+3} + H_2O \leftrightarrow An(OH)^{+2} + H^+$	-6.9	-7.6 ^a	-6.8
An(IV)			
$An^{+4} \leftrightarrow An^{+4}$	0	0	0
$An^{+4} + H_2O \leftrightarrow An(OH)^{+3} + H^+$	0.6	-0.54	0.55
$An^{+4} + 2H_2O \leftrightarrow An(OH)_2^{+2} + 2H^+$	0.6	-2.6 ^b	0.35
$An^{+4} + 3H_2O \leftrightarrow An(OH)_3^+ + 3H^+$	-2.3	-5.8 ^b	-6 ^c
$An^{+4} + NO_3^- \leftrightarrow An(NO_3)^{+3}$	1.95	1.47	1.9
$An^{+4} + 2NO_3^- \leftrightarrow An(NO_3)_2^{+2}$	3.22 ^c	2.3	3.2 ^c
$An^{+4} + 3NO_3^- \leftrightarrow An(NO_3)_3^+$	3.6 ^c	2.15 ^d	3.96 ^c
An(V)			
$AnO_2^+ + 4H^+ + e^- \leftrightarrow An^{+4} + 2H_2O$	17.43	7.55	10.21
$AnO_2^+ + H_2O \leftrightarrow AnO_2(OH) + H^+$	-11.3 ^a	-11.3	-11.3 ^a
An(VI)			
$AnO_2^{+2} + 4H^+ + 2e^- \leftrightarrow An^{+4} + 2H_2O$	33.25	9.04	36.10
$AnO_2^{+2} + H_2O \leftrightarrow AnO_2(OH)^+ + H^+$	-5.5	-5.25	-5.1
$AnO_2^{+2} + 2H_2O \leftrightarrow AnO_2(OH)_2 + 2H^+$	-13.2	-12.15	-11.52 ^d
$AnO_2^{+2} + NO_3^- \leftrightarrow AnO_2(NO_3)^+$	-0.07	0.3	0.522 ^d
$AnO_2^{+2} + 2NO_3^- \leftrightarrow AnO_2(NO_3)_2$	-7.5	-7.5 ^a	-7.5 ^a
SURFACE COMPLEXATION CONSTANTS			
An(III)			
$\equiv SOH + An^{+3} \leftrightarrow \equiv SAN^{+2} + OH^-$	-3.5 ^d	-5.13 ^d	-3.28 ^d
An(IV)			
$\equiv SOH + An^{+4} \leftrightarrow \equiv SAN^{+2} + OH^-$	13.89 ^d	11.25 ^d	13.78 ^d
An(V)			
$\equiv SOH + AnO_2^+ \leftrightarrow \equiv SANO_2 + OH^-$	-13.72 ^d	-13.72 ^d	-13.72 ^d
An(VI)			
$\equiv SOH + AnO_2^{+2} \leftrightarrow \equiv SANO_2^+ + OH^-$	-0.26 ^d	0.32 ^d	0.67 ^d

^a Morss et al., 2006^b Baes and Mesmer 1976^c Cross and Ewart 1991^d Estimated as part of this work

Thermodynamic constants for describing the sorption of actinides to glassy carbon surfaces are not available from the literature and had to be estimated prior to simulating EMS behavior. In most cases surface complexation for actinides in aqueous systems, like complexation in solution, is driven by the ion size of the sorbing actinide and the electrostatic interactions between them and the surface. As such, surface complexation follows very predictable behavior [Schwantes 2002; Schwantes 2004; Wang 2001], similar to that observed with solution complexation [Choppin 1983], in which the strength of binding of actinides (An) to charged surfaces generally follows the pattern



This pattern was quantified by several researchers [Wang 2001; Schwantes 2002; Schwantes 2004] for a number of different oxide surfaces (Figure 3).

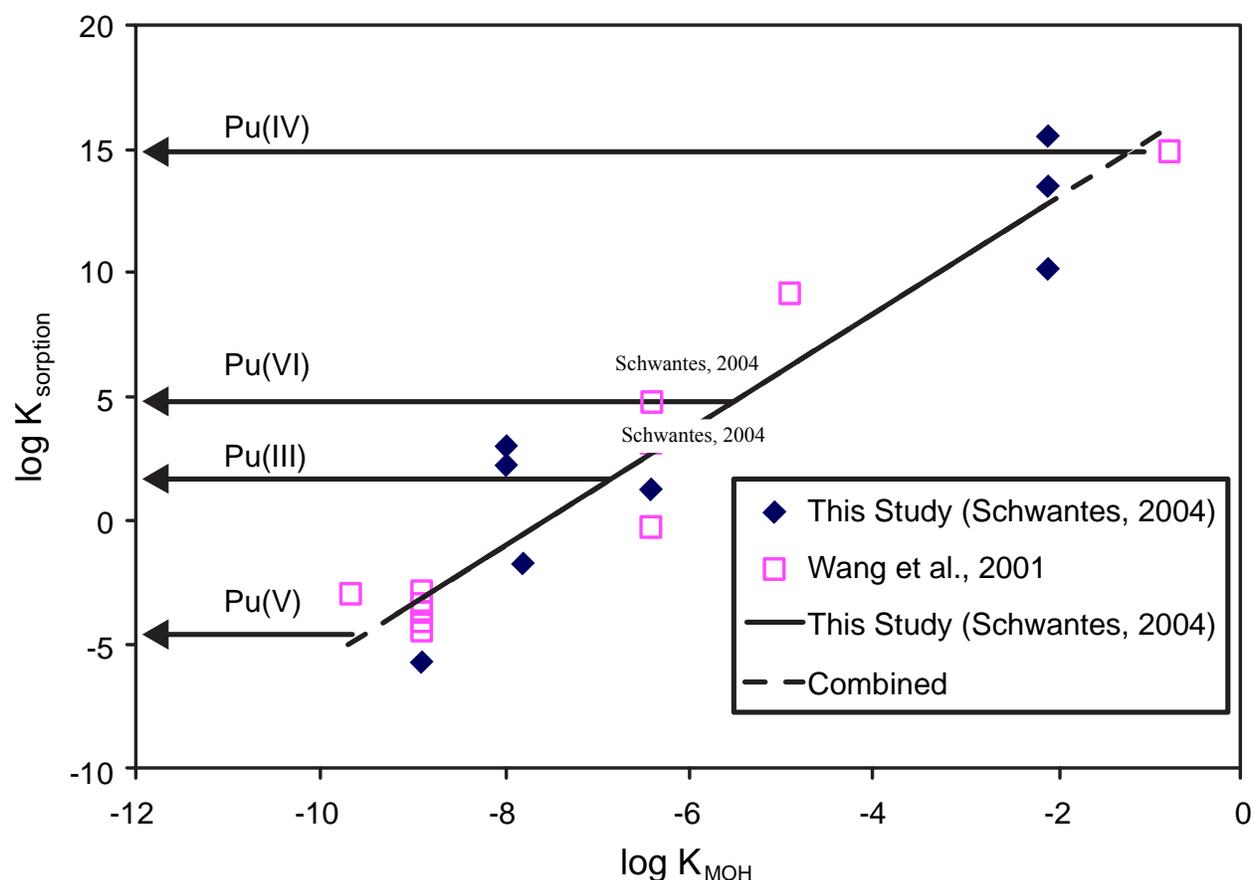


Figure 3. Surface complexation on mineral oxide surfaces as a function of first hydrolysis constants for actinide ions in aqueous systems [Schwantes 2004]

Evident in Figure 3, differences in the magnitude of the complexation constants between various oxide surfaces exist. However, the slope of the line in Figure 3 is relatively constant for specific oxides. The value of this slope describes the relative difference in strength of binding between the oxidation states of a particular actinide element. Since electrostatics are the main contributor to surface complexation reactions, it is a safe assumption that sorption for each oxidation state under acidic conditions will be driven by reactions involving the free (in the case of the III and IV oxidation states) and uncomplexed

linear di-oxo-cations (in the case of the V and VI oxidation states). Under more neutral and basic conditions, this assumption may not remain valid as the major ionic species of each oxidation state in solution (especially An(IV) species) would be dominated by hydrolyzed species. When this assumption is true, however, the relative magnitude of the first hydrolysis constant can be used as an indicator of the complexation strength of the free and uncomplexed linear di-oxo-cations. These values may be used to adjust the relative strength of binding for a number of actinides of a particular oxidation state using an altered form of the equation developed by Schwantes et al. [2002; 2004],

$$\text{Log}K_{\text{sorption}} = 2.32x(\text{Log}K_{\text{MOH}}) + X \quad (\text{Eq. 16})$$

where the Y-intercept (X) of the equation was adjusted to a value of 12.5 based on experimental observations in order to more accurately describe sorption to glassy carbon in the EMS system. Schwantes et al. (2004) found a strong correlation (R = 0.91) between modeled and measured values when this equation was applied to a variety of mineral oxides for actinides. Armed with this knowledge, relative constants describing the sorption of plutonium, uranium, and neptunium to glassy carbon were established and are presented in Table 1.

With the addition of surface complexation reactions to the model, redox of the actinide species is shifted towards the dominant surface species.

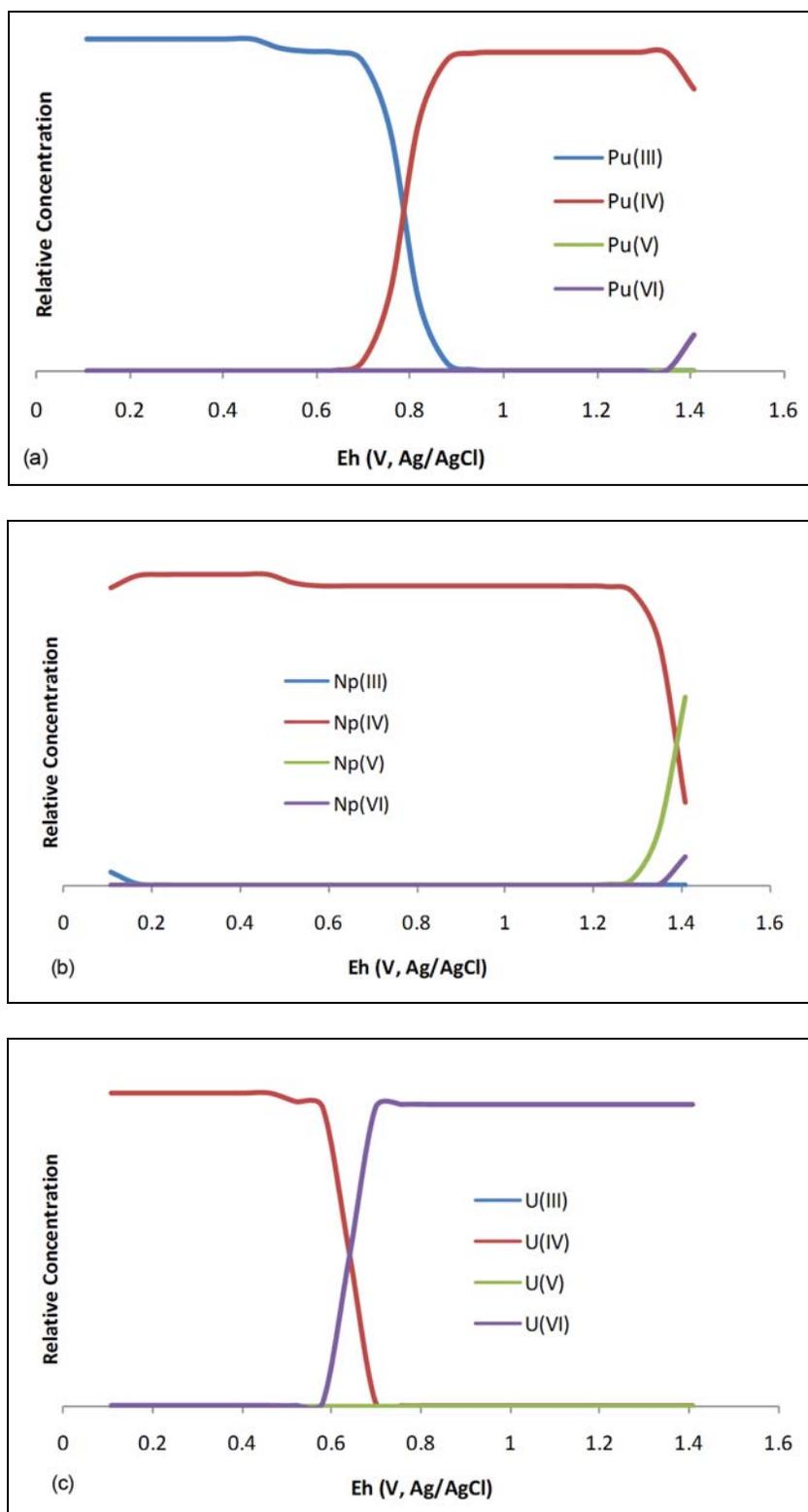


Figure 4 summarizes these shifts for plutonium, neptunium, and uranium.

3.2 Comparison of Experimental Observations and Model Simulations

Cell potentials and typical behavior observed during EMS separations optimized for pre-separation of plutonium and uranium are presented in Figure 5 and Figure 6, respectively. Also provided in these figures are results from reactive transport simulations of the EMS processes. Comparisons between modeled and measured results suggest that differences in the strength of surface complexation between the oxidation states of plutonium and uranium are the main mechanisms at work during EMS. Additionally, under optimized conditions, these comparisons suggest kinetic effects are not important during EMS, likely due to the drastic over-potentials applied to the cell in order to drive actinides between the reduced (III, IV) and oxidized (V, VI) states.

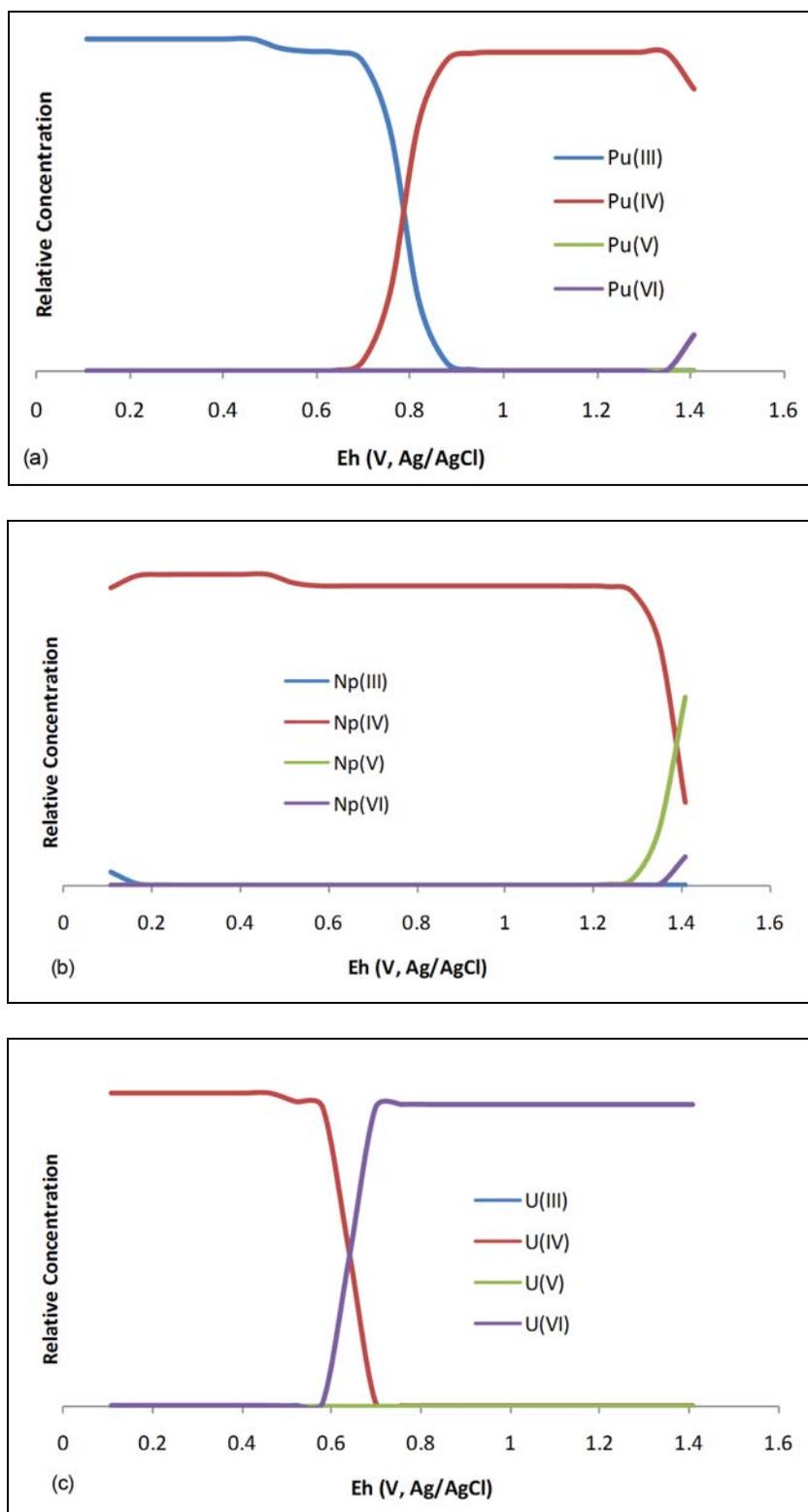


Figure 4. Redox distribution in 2% nitric acid of (a) plutonium, (b) neptunium, and (c) uranium in the presence of glassy carbon sorbing surface as a function of Eh

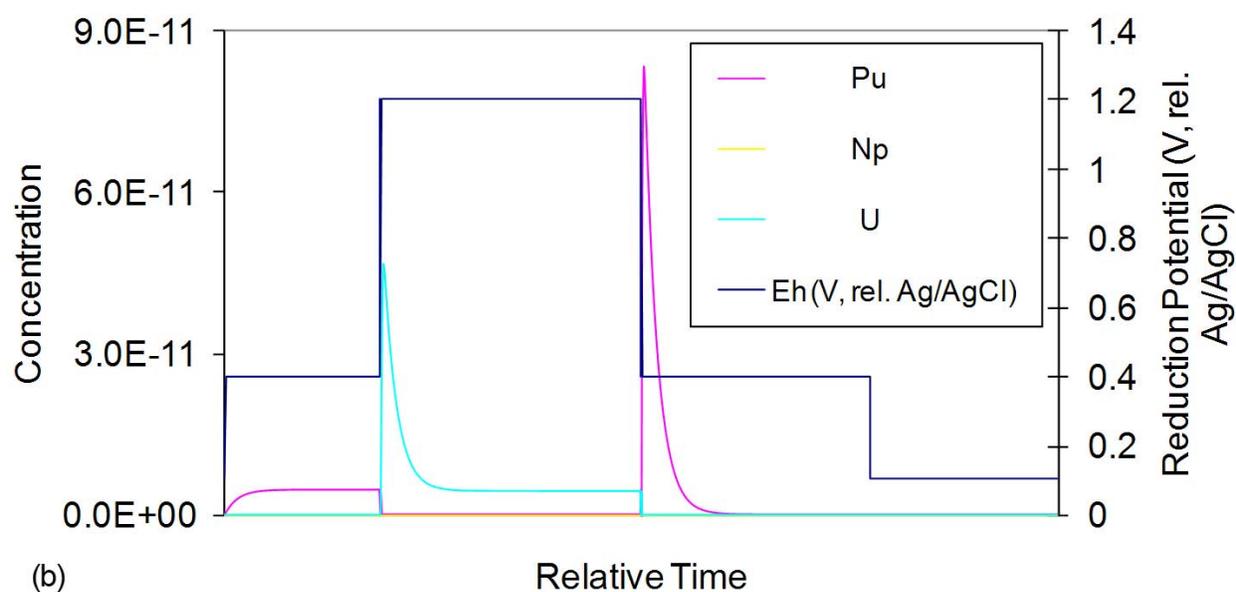
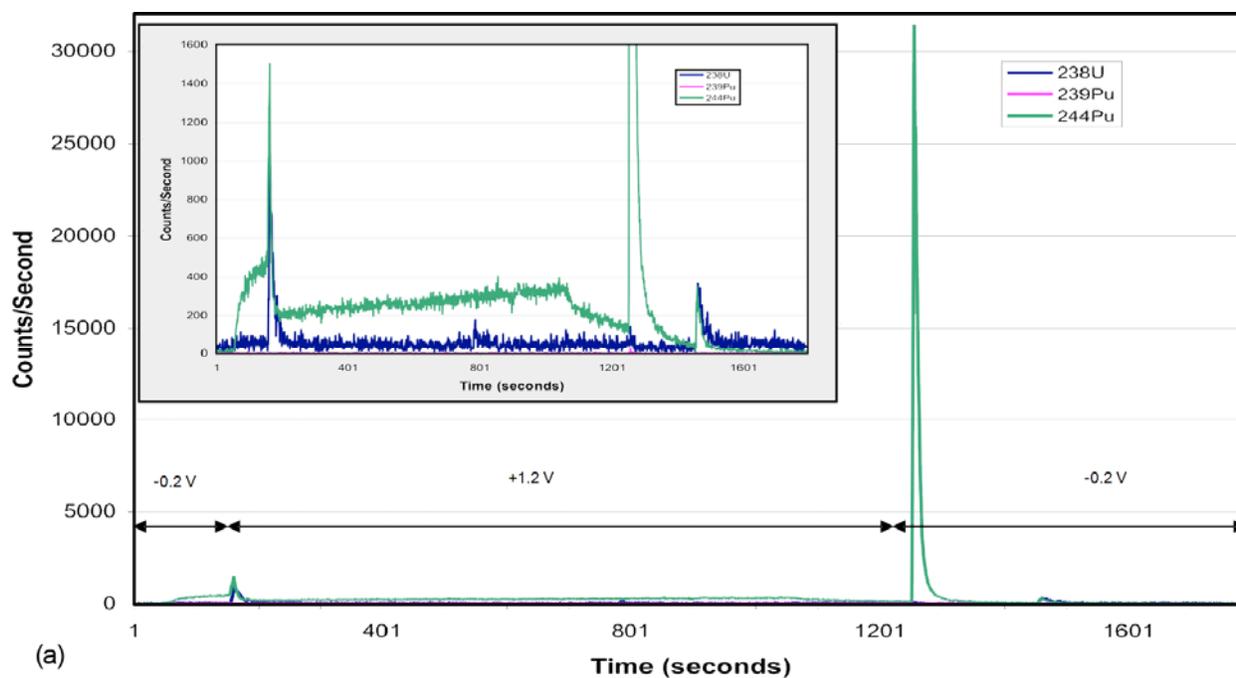


Figure 5. (a) Experimental results of EMS showing selective 70-fold plutonium pre-concentration from a solution containing both plutonium (4 ppt) and adventitious uranium [Schwantes In Press]. (b) Results from model simulations.

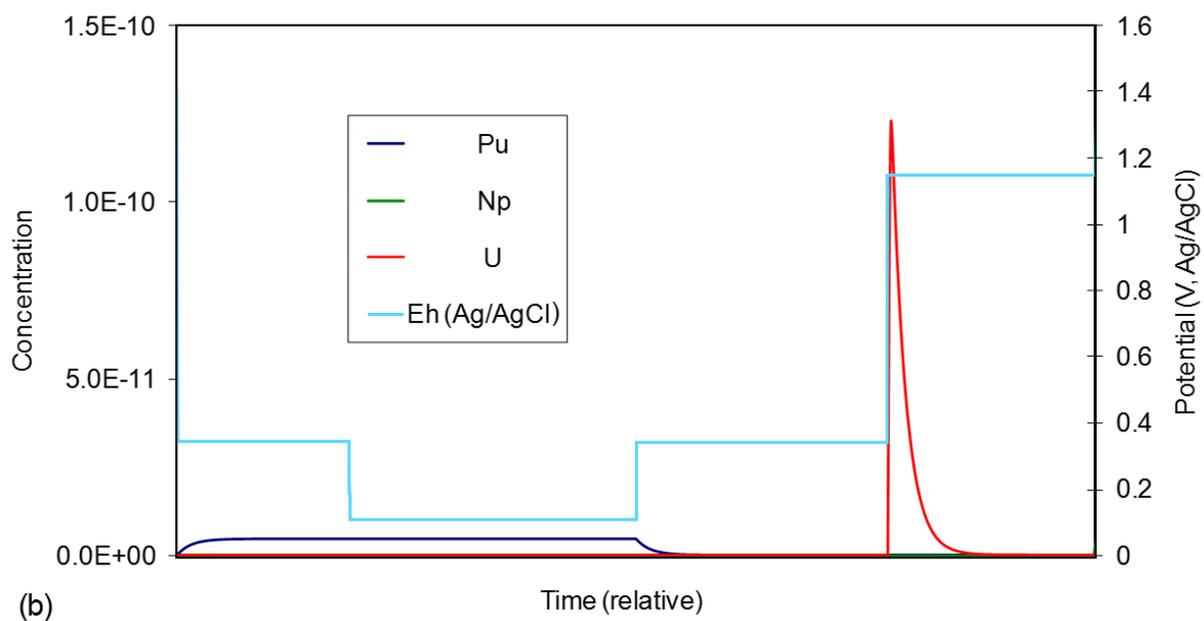
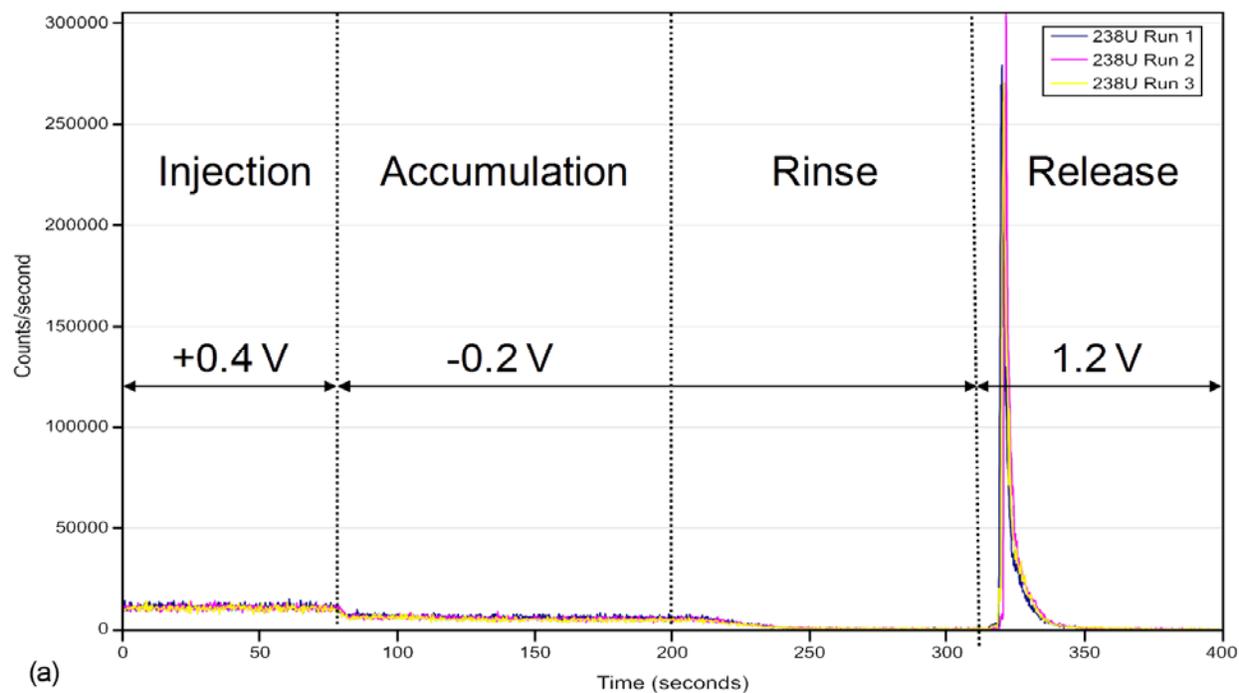


Figure 6. (a) Experimental data showing the three step process for accumulation and release of uranium [Schwantes In Press]. (b) Results of model simulations.

3.3 Using Model Simulations to Direct Laboratory R&D Associated with EMS

To date, EMS has only been applied successfully to the pre-separation of plutonium and uranium. Attempts to apply EMS to the pre-separation of neptunium prior to ICP-MS analysis have thus far been unsuccessful. Simulated runs optimized for plutonium and uranium pre-separation (E_H between -0.2 and 1.2 volts) roughly replicate the experimentally observed behavior for neptunium under these conditions, predicting that the reduction potential swing under these conditions was insufficient to shift the dominant neptunium species away from surface species controlling accumulation onto the glassy carbon electrode. Simulations were also conducted outside the bounds of what has been experimentally tested in the laboratory to date in an attempt to identify conditions suitable for the pre-separation of neptunium using EMS. Select results from these simulations conducted under slightly higher release potential are shown in Figure 7. These simulations suggest it may be possible to selectively pre-separate neptunium using EMS under such conditions.

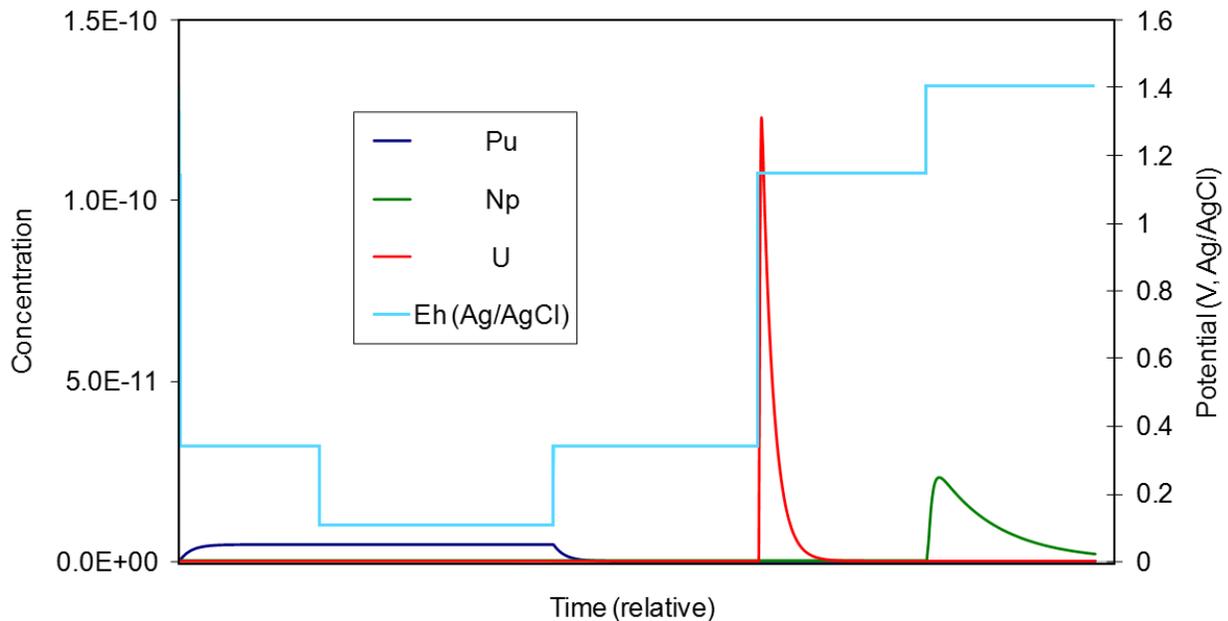


Figure 7. Model investigations suggesting conditions suitable for neptunium separation using EMS

4.0 Conclusions

This report summarizes the development and results generated from a mechanistic model designed to simulate EMS of actinide elements, an advanced on-line separation method currently under development at Pacific Northwest National Laboratory. These model simulations compared well with experimental observations, suggesting the major chemical species and reactions controlling behavior within the system were adequately represented in the model. In addition, the model was used to simulate conditions for EMS not yet tested in the laboratory that might be suitable for pre-separation of neptunium. Despite the fact that relatively inaccurate, estimated, values for surface complexation constants were used here, these simulations illustrate the utility of mechanistic models for directing R&D activities related to advanced separations methods for the actinides. Future work needs to be done to develop more accurate constants and models for accurately simulating a wider variety of separations techniques.

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