Application of a Site-Binding, Electrical, Double-Layer Model to Nuclear Waste Disposal

**J. F. Relyea
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September 1981

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APPLICATION OF A SITE-BINDING, ELECTRICAL,
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DISPOSAL

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SUMMARY

A site-binding, electrical, double-layer adsorption model (Davis, James and Leckie 1978) has been applied to adsorption of Cs for both a montmorillonite clay and powdered SiO_2 . Agreement between experimental and predicted results indicates that Cs^+ is adsorbed by a simple cation-exchange mechanism.

Further application of a combination equilibrium thermodynamic model and site-binding, electrical, double-layer adsorption model has been made to predict the behavior of U(VI) in solutions contacting either the montmorillonite clay or powdered SiO_2 .

Experimentally determined U solution concentrations have been used to select what is felt to be the best available thermodynamic data for U under oxidizing conditions. Given the existing information about the probable U solution species, it was possible to determine that UO_2^{+2} is most likely adsorbed by cation-exchange at pH 5. At higher pH values (pH 7 and 9), it was shown that $\text{UO}_2(\text{OH})_2^0$ is probably the most strongly adsorbed U solution species.

It was also found that high NaCl solution concentrations at higher pH values lowered U concentrations (either because of enhanced sorption or lowered solubility); however, the mechanism responsible for this behavior has not been determined.

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INTRODUCTION

Mechanistic and empirical sorption models are needed to perform safety assessments and predict the long-term fate of radionuclides in deep geologic nuclear-waste repositories. Defensible empirical data and an understanding of controlling mechanisms are needed to ensure the reliability of model predictions. Values for radionuclide retardation factors selected for existing assessment models are almost always intentionally low (conservative), because retardation processes are not completely understood and few field data are available. Travel times predicted using conservative retardation factors are probably much less than the actual radionuclide travel times (which can be verified only on a geologic time scale).

Present methods for the collection of radionuclide retardation data rely on laboratory experiments that are characterized by short times (less than a year), short path lengths (less than a meter) and small samples (less than a kilogram). The applicability of scaling these laboratory results to realistic time frames (thousands of years) and path lengths (kilometers) has not yet been shown.

The degree to which data obtained through laboratory and field tests are applicable to events over centuries can be determined by comparing these results with available equilibrium geochemical models and mechanistic sorption models. Maximal equilibrium radionuclide concentrations can be predicted using sufficient data on 1) site-specific aquifer characteristics (mineralogy, surface area, cation exchange capacity); 2) the chemical composition of groundwater, and 3) thermodynamic data describing the radionuclide solution chemistry and solid phases. Any radionuclide sorption on solid surfaces would then result in radionuclide concentrations below the maximal concentration predicted by equilibrium thermodynamic solubility models.

Not all of the needed thermodynamic data are available. However, if the available thermodynamic and mechanistic models are used in conjunction with solubility and retardation experiments, valuable information concerning reactive solute species and retardation mechanisms can be obtained. Expected

behavior can be compared to behavior observed experimentally to confirm the postulated mechanisms, to indicate another possible mechanism, or to show the need for more study to model the observed behavior.

Conclusive assessments of the safety and performance of nuclear waste repositories cannot be made until more reliable site-specific hydrologic and retardation data are gathered and a better understanding of adsorption mechanisms is acquired. The physical and chemical variability along each site-specific flow path over the long time frames involved must be addressed to establish the range of conditions that a radionuclide should encounter during transport. With this supporting information, mechanistic and empirical studies of radionuclide behavior, coupled with available thermodynamic predictions, can then be used to provide the needed retardation data.

The objective of this report is to describe the application of a combined geochemical and sorption model to the study of radionuclide retardation mechanisms for the prediction of radionuclide behavior over the long time frames required for isolation of nuclear waste.

SORPTION MODEL

The site-binding, electrical, double-layer model used in this study is described in detail by Silva et al. (1980) and Davis, James and Leckie (1978). For this reason, the model will be described only briefly in this report.

Most solid materials acquire a surface charge when placed in contact with a polar solvent such as water. The net charge may be positive, negative or neutral (point of zero charge), depending on the nature of the solid and solution compositions, particularly the pH. The most common mechanism for a surface to obtain a net electrical charge is through the uptake or release of potential determining ions on the surface (e.g., H^+ or OH^-). Charged surfaces tend to adsorb ions of opposite charge to maintain electrical neutrality and thus develop an electrical double layer. Permanent charges may also be present on solid surfaces because of isomorphous substitution in the crystal structure, such as Al^{+3} substituting for Si^{+4} or Fe^{+2} for Al^{+3} . The permanent charges

are treated as ionizable sites in the model presented here. If a surface is assumed to have only one kind of ionizable site, two reactions determine the surface charge:

where S in the equations refers to the surface to which the oxygen is bonded, and the subscript, s, refers to an ion at the surface (but not adsorbed) and differs from an ion in bulk solution by the amount of energy needed to move the charged ion across the difference in electrical potential between the surface and bulk solution. K_{a1} and K_{a2} are the surface ionization constants for these two dissociation reactions.

Normally, when a supporting electrolyte is present, ions other than H^+ balance the surface charge. If the solution contains only NaCl, the reactions describing the cation/anion charge balance are:

The electrical work needed to bring an ion from bulk solution to the charged surface results in a difference in activity for that ion at the two different positions. The model makes this correction so that the reaction constants can be related to quantities measured in solution. In a normal multicomponent groundwater, other cations and anions are found. These may be treated by writing equations similar to (3) and (4).

Exchange reactions such as Na^+ for H^+ can then be written as:

The constant $K_{Na/H}$ is frequently referred to as the selectivity coefficient. If more than one kind of exchange site exists on the surface, another set of equations similar to Equations (1) through (5) can be added to the model.

The resulting set of equations can then be solved algebraically to predict both the solution concentration and surface concentration for a particular element. If a distribution coefficient (K_d) is needed, the K_d may be calculated in a straightforward manner once these two concentrations are known. However, the already available solution and surface concentrations may be more valuable for radionuclide transport modeling than the K_d alone. The use of K_d in transport modeling is discussed in the WISAP technical progress report for FY-77 (PNL-2642).

Estimates of the surface ionization constants (K_{a1} and K_{a2}) are made from acid and/or base titrations of the adsorbing solids over a suitable range of electrolyte concentrations. Naturally, care must be taken that the pH range during titration does not extend past the range in which the solid phase is stable. The selectivity coefficients that describe the exchange of one cation (or anion) for another (for example Cs^+ exchange with Na^+) must also be determined experimentally or calculated from existing data for the system of solids and solutions being studied.

GEOCHEMICAL-SORPTION MODEL

Perhaps the most important aspect of this sorption model is that it is compatible with thermodynamic geochemical models. The surface ionization and exchange equations are written in the form of chemical reactions with their respective equilibrium constants. At the Lawrence Berkeley Laboratory, this adsorption submodel has been included in MINEQL (a computerized thermodynamic code developed by Westall, Zachary and Morel 1976) so that precipitation, dissolution, complex-ion formation, oxidation-reduction, and adsorption reactions can be considered simultaneously in a single geochemical model. If the initial surface and solution ion concentrations are known, a radionuclide may be added to the system, and its distribution between the solid and solution phases can be predicted.

Figure 1 shows a comparison between Cs^+ K_d values determined experimentally and those predicted by MINEQL for Belle Fourche clay (a montmorillonite) over a wide range of pH and NaCl solution concentrations. The dashed curve was calculated using the activity correction for the difference between bulk solution and surface potentials; the solid line was calculated without the correction. The predicted K_d values for Cs^+ exchange with Na^+ show a good correlation with the experimental data. It can be seen that the inclusion of the activity correction term (dashed line) did little to improve the fit.

Adsorption of Cs^+ on SiO_2 powder is shown in Figure 2. With the batch method used, the relative error for small K_d values is large. Again, the activity correction did little to improve the fit of experimental and predicted results. Below pH 7 the observed and predicted values for Cs sorption on quartz data deviate, but fair agreement is found in the environmentally important range, pH 7 to pH 10.

FIGURE 1. Log Distribution Coefficient (K_d) Versus pH for Cs and Belle Fourche Montmorillonite. Initial Cs^+ concentration = 1.01×10^{-7} M

FIGURE 2. Log Distribution Coefficient (K_d) for Cs Adsorption Versus pH on Quartz. Experimental data are shown by the solid points and uncertainty in the measured K_d values is shown by the vertical lines.

THEORETICAL AND EXPERIMENTAL PROGRAM

Currently, it is believed that sufficient data are available for making solubility and complexation predictions for uranium in the environment. The first step is to verify that predicted solution concentrations and species agree with experimental data. In other words, data from several sources can be compared with experimental results to ensure that the best data are chosen for the thermodynamic data base to be used as input for later model predictions.

If the thermodynamic model based on solubility and complex formation adequately depicts the solution behavior of a radionuclide, a solid-phase adsorber such as SiO_2 or a clay can be added to the system, and the coupled adsorption-thermodynamic model can be verified experimentally for that substrate. If the observed solution concentrations do not agree with the predictions after known adsorption mechanisms have been taken into account, additional mechanisms for adsorption or precipitation can then be determined and put into the coupled model.

Experimental work in progress at Lawrence Berkeley Laboratory (LBL) with U present initially as UO_2^{+2} has been conducted on SiO_2 (min-u-sil, a powdered quartz) and Belle Fourche montmorillonite. Solution variables are NaCl concentration (1.0 M, 0.1 M, 0.01 M and 0.001 M); CO_3^{-2} (10^{-4} M and no CO_3^{-2}), initial UO_2^{+2} concentration (10^{-4} M, 10^{-6} M and 10^{-8} M) and pH (5, 7 and 9).

Predictions of total U concentrations were made using the combined adsorption model, MINEQL, with thermodynamic constants from Langmuir (1978) and Lemire and Tremaine (1980). The Lemire and Tremaine data set includes constants for the formation of $\text{UO}_2(\text{OH})_2^{\circ*}$ and $(\text{UO}_2)_3(\text{OH})_7^-$, which are missing in Langmuir's data base. The dashed lines in Figures 3 and 4 are made using Langmuir's data (for 0.01 M NaCl only), and the solid lines are made with thermodynamic constants from Lemire and Tremaine. Predictions

* $\text{UO}_2(\text{OH})_2^{\circ}$ is a neutral solution species not to be confused with the solid phase $\text{UO}_2(\text{OH})_2(\text{s})$, which may precipitate.

FIGURE 3. Log Uranium Solution Concentration Versus pH for Quartz. Numbers on the solid lines and data points refer to the various NaCl concentrations: 1 ● 0.001 M NaCl, 2 ◆ 0.01 M NaCl, 3 ▲ 0.1 M NaCl and 4 ■ 1 M NaCl.

FIGURE 4. Log Uranium Solution Concentration Versus pH for Belle Fourche Clay. Numbers on the lines and data points refer to the various NaCl concentrations as follows: 1 ● 0.001 M NaCl, 2 ◆ 0.01 M NaCl, 3 ▲ 0.1 M NaCl and 4 ■ 1 M NaCl.

were made at discrete values of pH (5, 6, 7, 8 and 9) and joined by straight lines to account for the "kinks" in the predicted curves.

Uranium solubility has not been verified in a separate experiment; however, adsorption of 10^{-4} M UO_2^{+2} by SiO_2 was predicted to be negligible. Ten milliliters of 10^{-4} M UO_2^{+2} contains one milliequivalent (meq) of UO_2^{+2} . Because the powdered quartz has a sorption-site concentration of about 0.02 meq/g, and only 0.1 g of the quartz was used for sorption in 10 ml of solution, there is an excess of UO_2^{+2} of about 500 times the theoretical SiO_2 sorption capacity. Thus, the predicted concentrations in Figures 3A and 3B are essentially predictions for the solubility of $\text{UO}_2(\text{OH})_2(\text{s})$ and may be compared to experimental results for deciding which thermodynamic constants are best suited to model U behavior. In the experimental system used, an initial UO_2^{+2} concentration of 10^{-4} M should cause precipitation of $\text{UO}_2(\text{OH})_2(\text{s})$. Between pH 5 and 7, positively charged U species should be dominant. Between pH 7 and 8, a minimum in solution U concentrations should be observed as the neutral species $\text{UO}_2(\text{OH})_2^0$ dominates. Above pH 8, the negatively charged species $(\text{UO}_2)_3(\text{OH})_7^-$ gives an increase in U concentration with increasing pH. Experimental results shown in Figures 3A and 3B generally follow this trend (predicted with thermodynamic data from Lemire and Tremaine (1980) shown in Figure 5). It should be noted that the omission of a complex [such as $\text{UO}_2(\text{OH})_2^0$ and $(\text{UO}_2)_3(\text{OH})_7^-$ from Langmuir's data set] can be as much a problem as an incorrect thermodynamic value. Once the major complex ion species are known (or suspected), efforts may be concentrated on determining the formation constants for those species, and constants for minor species may receive less emphasis.

The effects of CO_3^{-2} on U concentration are seen only at pH 9 because below this pH, most dissolved CO_2 is present in the bicarbonate form (HCO_3^-). At pH 9, however, the presence of 10^{-4} M CO_3^{-2} does seem to increase the total U concentration as would be expected with the formation of UO_2CO_3^0 .

Adsorption of UO_2^+ was not predicted to be a significant factor in limiting the concentration of U in the presence of SiO_2 , but adsorption of UO_2^{+2} by the montmorillonite was expected to be significant. When the initial U concentration is undersaturated with respect to $\text{UO}_2(\text{OH})_2(\text{s})$, adsorption is predicted to lower the U concentration only in the montmorillonite system at pH 5 and 7,

FIGURE 5. Uranium Solution Species in Equilibrium with $\text{UO}_2(\text{OH})_2(\text{s})$. Supporting electrolyte is 0.01 M NaCl. Initial U concentration equal to 1.0×10^{-4} M.

because carbonate solution complexes should predominate at pH 9. Figure 4 shows that an ion exchange adsorption mechanism may be operative at pH 5 in the montmorillonite system. Adsorption at pH 5 is highest when the ionic strength is lowest (10^{-3} M NaCl) and when competition between Na^+ and UO_2^{+2} for exchange sites is also low. At higher ionic strength (1.0 M NaCl), Na^+ saturates adsorption sites on the clay and Cl^- forms a complex ion, UO_2Cl^+ which should be less competitive with Na^+ for adsorption sites than UO_2^{+2} . Even so, the match between predicted and observed concentrations at pH 5 is not all that great. At pH 7 and 9 there is no match at all between predictions and observed results, suggesting that ion exchange of UO_2^{+2} is not the predominant sorption mechanism at these pH values.

Similar total U concentrations were observed at pH 7 and 9 in solutions containing either SiO_2 or Belle Fourche montmorillonite. Thus, the results cannot be explained by cation-exchange adsorption of UO_2^{+2} alone. The expected increase of U in solution with increasing NaCl concentration was not observed. From the above information it appears that a common adsorption mechanism (not ion exchange) is operative in both the SiO_2 and montmorillonite systems.

Thus far it has been assumed for the adsorption model that only the UO_2^{+2} ion is adsorbed. Several U solution species are present and several might be adsorbed to a greater extent than UO_2^{+2} . Adsorption of the UO_2CO_3^0 species is not likely because an increase in CO_3^{-2} concentration (Figure 4) is found to increase the U solution concentration, indicating that CO_3^{-2} reduces U sorption. Adsorption of UO_2Cl^+ is not a likely mechanism either, because the UO_2Cl^+ concentration decreases by a factor of ten for each unit pH increase, and the chloride complex is negligible at higher pH values (>7).

In these systems (SiO_2 and clay), the only remaining U species of any importance are the hydrolyzed forms of UO_2^{+2} . Figure 6 shows the dominant solution species with total U = 10^{-8} M. Two complexes of U may be adsorbed: UO_2OH^+ and $\text{UO}_2(\text{OH})_2^0$.

It is not surprising that the dominant adsorption mechanism may change with increasing pH. James and Healy (1972) have shown that adsorption of several cations is abruptly enhanced as hydrolysis occurs and the ionic charge

FIGURE 6. Uranium Solution Species with Initial U Concentration Equal to 1.0×10^{-8} M. Supporting electrolyte is 0.01 M NaCl.

of the solute metal is lowered. It has also been suggested that the environment around surface-bound oxygen atoms ($-\text{SiO}^-$) and aqueous OH^- groups are similar (Stumm and Morgan 1970). This raises the possibility that a cation may form a surface complex with an $-\text{SiO}^-$ group analogous to aqueous OH^- as the pH is increased and hydrolysis becomes important. Thus, up to pH 5, ion exchange may be the dominant adsorption mechanism for UO_2^{+2} . As the pH approaches 5.5 to 5.9, the solution species $\text{UO}_2(\text{OH})^+$ and UO_2^{+2} become equal in concentration. However, the second hydrolysis occurs at only a slightly higher pH than the first, and $\text{UO}_2(\text{OH})_2^0$ soon becomes the dominant species. We might then expect that the mechanism for U adsorption could be the formation of complexes with surface-bound oxygens in competition with hydrolysis complexes formed in solution.

To model the surface complexation adsorption mechanism, an equation for each reaction must be written:

and

These two equations were included in the model, and the reaction constants (K_1 and K_2) were varied by trial and error to obtain the best fit to the experimental data. $\log K_2 \approx 4$ gave the best fit and K_1 was of minor importance. The data from Figures 3D and 3F are replotted in Figures 7 and 8, respectively, and the model predictions for 0.001 M NaCl and 1 M NaCl as the supporting electrolyte solutions are shown by the solid lines.

The empirical sorption model for U on SiO_2 shown in Figures 7 and 8 represents the observed sorption much better than the model used for predictions shown in Figure 3. Results from the empirical model indicate that a neutral species $\text{UO}_2(\text{OH})_2^0$ is highly adsorbed by the surface. James and Healy (1975) hypothesized that Cd adsorption by TiO_2 at pH values above 7 was mainly due to strong adsorption of $\text{Cd}(\text{OH})_2^0$. Schindler et al. (1976) later hypothesized that Cu(II), Cd(II), and Pb(II) may form bonds with two surface sites

FIGURE 7. Observed and Predicted U Concentrations After Adsorption on SiO_2 . Data are replotted from Figure 3D. New predictions (solid lines) were made by assuming the major adsorbed species was $\text{UO}_2(\text{OH})_2^\circ$.

at pH values where these divalent cations would normally hydrolyze in solution. [The model proposed by Schindler et al. (1976) allows adsorption of the unhydrolyzed divalent cation, but adsorption depends on the hydrolysis constant for that cation.] Davis and Leckie (1978) used the same model (site-binding, electrical, double-layer) that is used for this work, and found that adsorption of Ag(I) on amorphous iron oxyhydroxide could be better described if $\text{Ag}(\text{OH})^\circ$ and Ag^+ were both adsorbed than if Ag^+ alone was assumed to sorb.

Thus, the hypothesis that $\text{UO}_2(\text{OH})_2^\circ$ is the major adsorbed species in this work is not without precedent. The exact mechanism for the extensive adsorption of U on SiO_2 at pH 7 is presently unknown and, as stated by Davis and Leckie (1978), "Careful studies of the kinetics of surface reactions will be necessary to determine whether hydrolysis occurs first in solution or at the surface following adsorption of an aquo metal ion."

Another aspect of U behavior in both the SiO_2 and clay system that requires more research is the influence of NaCl on U concentrations. Complexation by Cl^- to form UO_2Cl^+ and competition with Na^+ for exchange sites should reduce U adsorption at higher NaCl concentrations. At pH 7 and 9 in the SiO_2

FIGURE 8. Observed and Predicted U Concentrations After Adsorption on SiO_2 . Data are replotted from Figure 3F. New predictions (solid lines) were made by assuming the major adsorbed species was $\text{UO}_2(\text{OH})_2^\circ$.

system and at pH 9 with the clay, the higher NaCl concentrations seem to enhance adsorption of U instead of reducing the adsorption as would be expected. It is possible that dispersion of the suspended particles at low NaCl concentrations gives high values for U in solution because of adsorbed U on those particles; but, this is unlikely because all samples were filtered through a 0.2- μm membrane before counting. It is also possible that a solid phase other than $\text{UO}_2(\text{OH})_2(\text{s})$ may limit U solubility in these systems. Rai and Serne (1978) have postulated that Na_2UO_4 may control uranium solubility under the conditions here. The data shown in Figures 3A and 3B, however, indicate that $\text{UO}_2(\text{OH})_2(\text{s})$ is indeed a likely candidate solid phase that places an upper limit on the U solution concentration. The effect of high NaCl concentration

on U concentrations will require further study because of the possibility of a nuclear waste repository being placed in bedded or dome salt. Lowered solubility or enhanced adsorption of U in salt brine or bittern would greatly reduce the release rate of U from a repository and thus lessen the consequences of both U and the long-lived daughter, Ra-226, in the accessible environment.

SUMMARY AND CONCLUSIONS

The combined use of an equilibrium thermodynamic chemical model and the site-binding, electrical, double-layer adsorption model has led to predictions about dissolved U concentrations following sorption onto a montmorillonitic clay and onto SiO_2 from solutions varying from 10^{-8} M to 10^{-4} M initial UO_2^{+2} concentrations.

These predictions have been checked experimentally. In the case where U sorption was calculated to be negligible (10^{-4} M initial UO_2^{+2} in an SiO_2 suspension), the results have served to test the thermodynamic solubility and complexation data base and provide a basis for selecting what is felt to be the best available data.

This approach also aids in determining the conditions for which a simple electrostatic ion exchange mechanism is the dominant adsorption mechanism. When the proposed mechanism is found to be invalid (such as is the case for UO_2^{+2} sorption at pH 7 and 9), the chemical model is still a valuable guide for determining what solution species or surface characteristics may be responsible for the unexpected behavior.

It was assumed that the hydrolyzed solution species UO_2OH^+ and $\text{UO}_2(\text{OH})_2^\circ$ were adsorbed at the higher pH values. By varying the reaction constants for the surface complexes that might be formed by the two hydrolyzed species, it was found that U sorption could be modeled empirically. The results of the empirical modelling suggest that the neutral species $\text{UO}_2(\text{OH})_2^\circ$ is strongly adsorbed.

High NaCl concentrations at pH 7 and 9 with SiO_2 and at pH 9 with the clay were unexpectedly found to cause lower U solution concentrations, compared to U concentrations in dilute NaCl. The implication is that either U sorption is enhanced or U solubility is lowered in high-ionic-strength NaCl solutions. Either of these two effects will reduce the hazard of U to the environment in a bedded salt or salt dome repository. Continued efforts are needed to 1) identify and model the mechanism responsible for enhanced sorption of U observed at pH ≥ 7 , and 2) identify the mechanism responsible for the inverse relationship between solution NaCl and U concentrations.

This study is an important step in determining the mechanisms responsible for the adsorption of uranium (as well as plutonium, neptunium and other radionuclides that form oxycations or complex ions with ligands in groundwater). The concept will be extended to other cation-surface complexation reactions in the future.

If the mechanisms that control the solution concentration of a radionuclide are known (e.g., an adsorption or precipitation reaction) and equilibrium expressions for those mechanisms can be written, the concern over short times and path lengths encountered in laboratory experiments can be discounted. As long as the environment is not altered, the equilibrium of a solution-surface-radionuclide system will not change in time or space, and predictions based on the knowledge of sorption and thermodynamic processes will be invariant. If laboratory experiments using appropriate environmental conditions are performed until equilibrium is attained, then the results should be valid for predicting actual events in the field.

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