

## **DIFFUSE-LAYER SURFACE COMPLEXATION MODELING TO DESCRIBE PARTITIONING OF URANIUM(VI) BETWEEN THE SOIL AND GROUNDWATER IN THE 200 WEST AREA OF THE HANFORD SITE, WASHINGTON**

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### **ABSTRACT**

MSE Technology Applications, Inc. (MSE), in cooperation with Fluor Hanford, Inc. (FHI) is conducting a study in the 200-West Area of the Hanford Site, Washington, to describe partitioning of hexavalent uranium [U(VI)] between the soil and groundwater in the unsaturated and saturated sediments associated with the 216-U1/U2 Cribs in the 200-West Area of the Hanford Site.

To describe U(VI) partitioning, hence also its mobility, MSE developed a geochemical model that quantifies both the amount of U(VI) in solution and the amount of U(VI) sorbed to the soil and/or precipitated out of solution. The geochemical model predicts U(VI) partitioning by incorporating diffuse layer surface complexation. Surface complexation is the formation of chemical complexes consisting of solid mineral phases and ions in solution. The use of surface complexation models requires understanding the chemical and physical properties of the soil and groundwater and their interactions occurring between the two.

MSE calibrated the geochemical model using a series of laboratory batch tests that quantified U(VI) partitioning. During calibration, input parameters for the geochemical model were adjusted to produce an acceptable correlation between the model and laboratory data. The calculated root mean squared errors between the model and laboratory data ranged from 0.08 to 0.18.

After the geochemical model calibration, U(VI) partitioning was modeled for a new series of batch tests. The calculated root mean squared errors between the model and laboratory data for these tests were slightly higher. Values ranged from 0.06 to 0.48. The higher values may be a result of the inability of the model to deal with U(VI) precipitation kinetics.

Based on the results of this study, MSE found that U(VI) adsorption is greatest when the solution pH ranges from 4 to 7. Uranium precipitation is the dominant mechanism for removal of uranium from solution at higher pH values ( $\text{pH} < 8$ ).

The quality of the model validation results clearly show that the model can be used to describe U(VI) partitioning for a range of conditions outside those used for the initial model calibration. However, the model predictions could be improved if kinetics of precipitation are considered.

### **INTRODUCTION**

MSE Technology Applications, Inc. (MSE), in cooperation with Fluor Hanford, Inc. (FHI) is improving the understanding of uranium partitioning between soils and groundwater in the 200-UP-1 Operable Unit of the 200-West Area of the Hanford Site, in Washington State. The objective of MSE's project is to quantify uranium partitioning in the unsaturated and saturated soils associated with the 216-U1/U2 Cribs.

## GEOCHEMICAL MODEL

MSE developed a geochemical model that quantifies uranium partitioning (sorption and/or precipitation) using diffuse layer surface complexation. Surface complexation models require understanding the chemical and physical properties of the soil and groundwater and their interactions. These reactions control the formation of chemical complexes between solid mineral phases and ions in solution. Surface complexation models can describe changes in partitioning as a function solution chemistry; and therefore are well suited to modeling partitioning in a system with changing pH and soil/groundwater chemistry.

Based on previous studies, MSE considered the following parameters significant to uranium partitioning: solid and aqueous species; carbon dioxide/carbonate concentrations; aqueous, dissolution, and precipitation reactions and their associated thermodynamic data; surface complexation sorbent properties; and surface complexation reactions and their associated thermodynamic data. These parameters were defined through laboratory analyses and relevant literature values.

Data used for the geochemical model included the type and concentration of aqueous components, applicable aqueous and precipitation/dissolution reactions, and the parameters and reactions for surface complexation. These reactions are defined through equilibrium constants, enthalpy values, and stoichiometric coefficients. The equilibrium constants and enthalpy values for the model make up the thermodynamic database, which was taken mainly from MINEQL+, a Windows™ based chemical equilibrium modeling system. MINEQL+ was derived from the MINTEQA2 [2] code. In addition, MSE also compiled thermodynamic data using information from professionals and recent studies on uranium adsorption.

The geochemical modeling efforts included the following ions:  $\text{Al}^{+3}$ ,  $\text{Ca}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{+2}$ ,  $\text{Mn}^{+3}$ ,  $\text{Na}^{+}$ ,  $\text{Si}^{+4}$ ,  $\text{U}^{+6}$ ,  $\text{CO}_3^{-2}$ ,  $\text{Cl}^{-}$ ,  $\text{F}^{-}$ ,  $\text{NO}_3^{-}$ ,  $\text{PO}_4^{-3}$ , and  $\text{SO}_4^{-2}$ . The model also allowed precipitation and dissolution of mineral species. Because the MINEQL+ geochemical model does not allow for finite amounts of solids to be initially present in the system, precipitation and dissolution of mineral species were modeled as dissolution of “fixed” solids (i.e., infinite supply) and precipitation of dissolved species.

For the geochemical model efforts, iron was considered the primary sorbent for U(VI). Specifically, MSE considered the iron species goethite ( $\text{FeO}\cdot\text{OH}$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), and magnetite ( $\text{Fe}_3\text{O}_4$ ) to be the primary sorbents. The concentration of sorbing sites in each soil sample was estimated using a citrate-bicarbonate-dithionite (CBD) extraction, laboratory analytical work, optical microscopy, and a review of literature [8]. MSE calculated the total concentration of sorbing sites as the sum of sorbing sites contributed by goethite, hematite, and magnetite.

Previous studies [5,9,10,11] have divided sorption sites on hydrous ferric oxide into two types: strong sites (SOH) and weak sites (WOH). Weak sites are the total reactive sites available for sorption of protons, cations, and anions; and, strong sites are a smaller set of high-affinity cation binding sites [11]. Both strong and weak sites were incorporated into MSE's geochemical model efforts. A strong site to weak site ratio of 1 to 30 provided the best fit for the geochemical modeling of the Hanford soils. This ratio falls within the range of strong and weak site densities reported in previous work [11].

Surface complexation equilibrium reactions used in the geochemical modeling efforts were compiled from numerous sources. Although multiple iron species were considered when calculating total sorbing site concentrations, limitations in the database prevented modeling sorption to the specific iron species. Consequently, the surface complexation reactions describe complexation to “generic” iron represented by goethite, hematite, and magnetite. Stability constants\* for the surface complexation reactions were derived for each Hanford soil modeled.

## Geochemical Model Calibration

Calibration of the geochemical model was accomplished by adjusting the surface complexation parameters such the model achieved a best fit with measured laboratory data. Laboratory data were obtained through a series of batch tests designed to assess U(VI) partitioning between the Hanford soils and batch test solution over a range of pH values.

Batch tests were performed using 5 soil samples (101B-Hanford Unit 1, 104B-Hanford Unit 2, 106B-Hanford Unit 2, 112B-Plio-Pleistocene Caliche, and 119B-Upper Ringold) obtained during the drilling of borehole 200-W19-43 in the 200-West Area. The calibration batch tests, completed under ambient atmosphere conditions, used only one uranium concentration (approximately 2.5 mg/L). Sub-solutions of uranium-spiked water were prepared by adjusting the pH with either hydrochloric acid for lower pH values or sodium hydroxide for higher pH values to achieve the desired (target) pH values (3 to 9). The percent of U(VI) that was removed from solution during the batch tests was calculated for each sample.

Results from the calibration batch tests and analysis of the calibration soil samples were used to define the geochemical model surface complexation parameters. To determine the sorbent site concentrations, expressed in per liter of solution, the solid to aqueous ratio used in the batch tests (10-g of soil to 40-mL of solution) as well as the 1 to 30 strong site to weak site ratio were considered. Uranium partitioning was modeled for each soil sample and compared to the U(VI) partitioning measured in the batch tests. The goodness-of-fit between the simulated and measured U(VI) adsorption data was evaluated quantitatively and qualitatively. For the quantitative evaluation, the goodness-of-fit between the results was determined by calculating the root mean squared error (RMSE) according to:

$$\text{RMSE} = \left[ \frac{1}{(n_d - n_p)} \sum_{i=1}^{n_d} \left( \frac{C - C'}{C_0} \right)^2 \right]^{1/2} \quad (\text{Eq. 1})$$

where  $n_d$  is the number of data points,  $n_p$  is the number of adjustable parameters or degrees of freedom,  $C$  is the measured concentration,  $C'$  is the predicted concentration, and  $C_0$  is the initial concentration. RMSE values calculated for the geochemical model calibration are shown in Table I.

Table I. Calculated RMSE values for geochemical model calibration

| Sample                          | RMSE |
|---------------------------------|------|
| 101B - Hanford Unit 1           | 0.08 |
| 104B - Hanford Unit 2           | 0.12 |
| 106B - Hanford Unit 2           | 0.10 |
| 112B - Plio-Pleistocene Caliche | 0.13 |
| 119B - Upper Ringold            | 0.18 |

## Geochemical Model Validation

The geochemical model validation was carried out by using the model to predict uranium sorption to soils that were not used for model calibration. The validation batch test process was very similar to the process used for the geochemical model calibration. Uranium adsorption data collected from the validation process was compared to the adsorption predicted by the geochemical model.

## Validation Batch Tests

The batch tests for validating the geochemical model were completed in July 2003. The validation batch tests were performed using soil samples 121 (Upper Ringold) and 124 (Ringold Unit E Gravels) acquired during the drilling of borehole 299-W19-43. Uncontaminated groundwater, used in the validation batch tests, was acquired from well 699-55-89, which is approximately 2 miles up-gradient of the study area. The well 699-55-89 water was spiked with uranyl-nitrate hexahydrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) to simulate uranium-contaminated water. The “initial” uranium concentration used for validating the geochemical model was approximately 1.4 mg/L ( $5 \times 10^{-6}$  M), which was similar to the concentration used in the additional calibration batch tests (2.5 mg/L or  $6.34 \times 10^{-6}$  mol/L). Batch tests were also performed using water with uranium concentrations that were approximately 20, 40, 60, and 100 times the “initial” concentration. Sub-solutions of the raw and spiked well water were prepared by adjusting the pH with either hydrochloric acid for lower pH values or sodium hydroxide for higher pH values to achieve the desired (target) pH values (3 to 10).

Parameters for modeling the validation batch tests were determined through analysis of the soils and aqueous portions of the batch test samples. Aqueous U(VI) concentrations from the spiked batch test samples were not examined until the geochemical model results were available. Sorbent site concentrations were calculated using CBD extract and optical microscopy results and took into account the solid to aqueous ratio used in the batch tests (10-g to 40-mL) as well as the strong site to weak site ratio of 1:30. Uranium adsorption/precipitation was predicted and compared to the U(VI) adsorption/precipitation measured in the batch tests. The goodness-of-fit between the predicted and measured U(VI) adsorption data was evaluated both quantitatively and qualitatively following the procedure used for evaluation the model calibration. RMSE values calculated for the geochemical model calibration are shown in

Table II.

Table II Calculated RMSE values for geochemical model validation

| Sample                        | U(VI) Concentration | RMSE |
|-------------------------------|---------------------|------|
| 121<br>Upper Ringold          | Initial             | 0.28 |
|                               | 20 x Initial        | 0.45 |
|                               | 40 x Initial        | 0.28 |
|                               | 60 x Initial        | 0.29 |
|                               | 100 x Initial       | 0.34 |
| 124<br>Ringold Unit E Gravles | Initial             | 0.06 |
|                               | 20 x Initial        | 0.35 |
|                               | 40 x Initial        | 0.28 |
|                               | 60 x Initial        | 0.48 |
|                               | 100 x Initial       | 0.44 |

## DISCUSSION

Overall, the geochemical model results show good agreement with measured results for each of the Hanford soils modeled. With the exception of a few points, simulated and measured results from the calibration samples showed the same general shape and adsorption values. RMSEs between the simulated and measured data ranged from 0.08 to 0.18. Soils with higher total surface site concentrations (e.g., sample 119B) show a greater ability to adsorb U(VI). The results also show that increased carbonate in the system leads to a decrease in U(VI) adsorption. U(VI) adsorption observed in the caliche sample (112B) was significantly different from the adsorption observed in the other calibration samples where the carbonate concentrations were much lower. These results agree with other studies [12] that

investigated how the type and concentration of iron species and the carbonate concentration control U(VI) adsorption.

Predicted and measured results from the validation samples showed slightly less agreement. RMSE values ranged from 0.06 to 0.48. The lowest error was observed for the “initial” uranium concentration samples. As the uranium concentration increased, i.e., the model was stressed, the error increased.

The higher values may be a result of the inability of model to deal with kinetics of precipitation. MINEQL+ is an equilibrium model, which by definition assume the system has reached equilibrium, and do not consider kinetics of reactions. Reaction rates for sorption and precipitation can differ significantly. Sorption often occurs on the order of seconds to hours, while precipitation often occurs at a much slower rate (days to years) [4]. Sorption and precipitation processes are also dominant in different pH regions. Sorption typically occurs over a low to mid pH range (pH 3 to 7). Precipitation is more dominant at higher pHs (above pH 9).

Predicted and observed results tended to have the most discrepancy in the higher pH range, where precipitation of U(VI) species may dominate the removal of U(VI) from solution. The predicted results typically over predict U(VI) removal from solution. Both the calibration and validation batch tests were performed over a time period of approximately 2 weeks. This amount of time may not have been sufficient for all precipitation to finish, i.e., bringing the system to complete chemical equilibrium.

## CONCLUSIONS

Previous studies into uranium adsorption have often involved the use of pure, synthetic iron matrices. The models produced in these studied were usually very good at predicting uranium adsorption. However, when these models were applied to natural soils, the predicted and observed results were often significantly different. Geochemical models for natural sediments are known to be difficult to fit because of the complexity of the solid matrix.

MSE applied a geochemical modeling process to a suite of natural sediments. Modeling results from validation soils and a uranium concentration similar to the concentration used to calibrate the modeling process suggest that geochemical modeling is applicable to the Hanford soils. RMSEs for the validation soils at the uranium concentration similar to the concentration used for calibration fell within the RMSE range obtained during the model calibration. In addition, even as the model was stressed by increasing the uranium concentration two orders of magnitude, RMSEs only increased about 2½ times.

No examples where surface complexation models were stressed to conditions outside of the initial calibration conditions (i.e., increasing uranium concentration) were found in the literature. MSE stressed the surface complexation models as part of the validation efforts and was able to obtain meaningful results. The results of increasing the uranium concentration on removal of uranium from solution suggest that in the pH range for sorption, the uranium that can sorb is removed during batch tests (predicted and observed results showed good agreement); but, in the pH range for precipitation, the uranium that can precipitate did not fully come to equilibrium (predicted and observed results showed less agreement). Considering the above, the predicted/observed fits achieved for the 7 Hanford soils are good.

## ACKNOWLEDGEMENTS

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## FOOTNOTES

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- \* Stability constant, applicable for a multi-sorbent matrix, is a cumulative constant calculated as a product of individual equilibrium constants. For the work reported in this paper the stability constant was derived by fitting the model to the batch test data.