# URANIUM PARTITIONING IN UNSATURATED AND SATURATED SEDIMENTS IN THE 200 WEST AREA OF THE HANFORD SITE, WASHINGTON

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## ABSTRACT

Uranium-contaminated wastewaters produced during historical operations in the 200 West Area of the Hanford Site, Washington, were often discharged to subsurface disposal cribs. In February 1985, the concentration of uranium and technetium-99 in the groundwater of the 200-UP-1 Operable Unit abruptly increased. A pump-and-treat system was installed to reduce the contaminant mass within the plume and minimize migration of uranium and technetium-99 from the 200 West Area. Monitoring data has shown that the pump-and-treat system is effectively removing technetium-99 from the groundwater. The pump-and-treat system has had less success remediating the uranium plume. Although it is providing hydraulic control, the ineffectiveness of the pump-and-treat system on the uranium plume remediation is attributed, in part, to the tendency of uranium to sorb to the soil. Consequently, the amount of uranium remaining in the soil as a potential source for the plume is not accurately known.

MSE Technology Applications, Inc. (MSE), in cooperation with Fluor Hanford, Inc. (FHI) is working to better understand the processes controlling uranium mobility in the 200-UP-1 Operable Unit. The objective of MSE's project is to develop a geochemical model that better defines the partitioning of uranium in the unsaturated and saturated soils associated with the 216-U1/U2 Cribs in the 200 West Area. The uranium-partitioning model is controlled by surface complexation processes.

To quantify uranium partitioning, MSE developed a geochemical model that incorporates diffuse layer surface complexation. The use of surface complexation models requires an understanding of the chemical and physical properties of the soil and groundwater and the interactions occurring between the two. The modeling approach used for this project combined the component additivity and generalized composite models. Surface site concentrations were estimated from the discrete iron phases observed in the soil samples. However, the equilibrium constants for sorption reactions were determined by fitting the model to the lab data, i.e., using a general composite approach.

The geochemical model was calibrated by comparing results from series of laboratory batch tests to the uranium adsorption/precipitation predicted by the geochemical model. Input parameters for the geochemical model were adjusted within reasonable bounds in order to produce an acceptable correlation between the simulated and measured data. After the geochemical model was calibrated, U(VI) adsorption/precipitation was predicted for a new series of batch tests. The conditions of the batch tests were modeled in order to verify that the geochemical model could predict U(VI) adsorption/precipitation for a different set of geochemical conditions.

## INTRODUCTION

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 uranium between the soil and groundwater in the unsaturated and saturated sediments. MSE proposed developing a geochemical model to define the partitioning of uranium in the subsurface as a function of site-specific geochemical conditions. The geochemical model will use surface complexation adsorption theory to improve estimates of uranium partitioning. Surface complexation is dependent upon the properties of the sorbent, which the uranium complexes to, as well as the geochemistry of the system. Geochemical

properties of particular interest include pH and the concentration of carbonate.

**Project Site Location**

The U.S. Department of Energy's (DOE) Hanford Site is located in south central Washington State (see Fig. 1) just north of the confluence of the Snake and Yakima Rivers with the Columbia River.
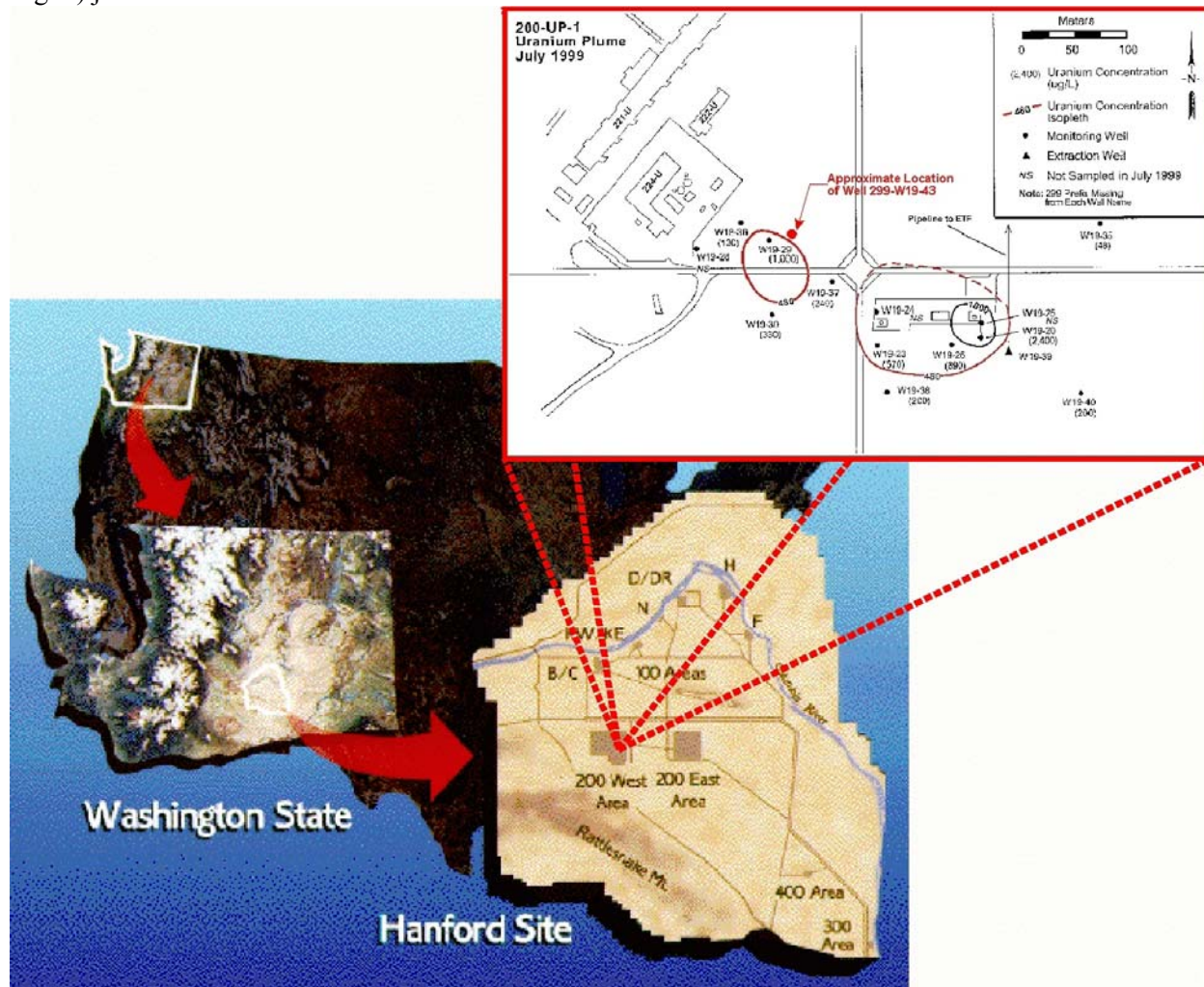


**Fig. 1.  Location of Hanford Site, project site location and uranium plume in the 200-UP-1**

**Operable Unit.**

The site covers approximately 1,518 square kilometers and is divided into a number of operational areas. MSE's project is related the 200 West Area which is located in the center of the Hanford Site. Specifically, the area of interest is the 200-UP-1 Groundwater Operable Unit just southeast of the Uranium Processing Plant (U-Plant).

**Contaminant History**

Historical operations of facilities in the 200 East and 200 West Areas included plutonium production processes and uranium recovery from process waste.  Some wastewaters contaminated with uranium and other pollutants were discharged to subsurface disposal cribs in the 200 West Area.  In February 1985, the

concentration of uranium and technetium-99 in the groundwater of the 200-UP-1 Operable Unit abruptly increased. The contamination of the groundwater has been primarily attributed to discharges to the 216-U1/U2 Cribs in the 200 West Area. Fig. 1 shows the approximate extents of the uranium plume from sampling data acquired in July 1999.

Currently, a pump-and-treat system is in place at the site. This system was designed to reduce the contaminant mass within the plume and minimize migration of uranium and technetium-99 from the 200 West Area. Analytical data from monitoring wells located within and around the contaminated groundwater indicate the pump-and-treat system is effectively removing the technetium-99 from the groundwater, however, it is not removing enough uranium from the groundwater to meet the compliance requirements for the site.

## PROJECT SCOPE

The objective of MSE's work was to better refine the conceptual model of uranium mobility in the 200-UP-1 Operable Unit. To accomplish this MSE chose to develop geochemical models, incorporating surface complexation, that could be used to describe the partitioning of uranium in the unsaturated and saturated soils associated with the 216-U1/U2 Cribs. Surface complexation was considered to be the key process controlling uranium partitioning. The goal of the modeling effort was to produce an acceptable correlation between predicted and observed concentrations of uranium in the groundwater. The factors expected to play a key role in uranium partitioning were identified through characterization of the soils from the site and a literature review. This information provided a basis for the geochemical modeling.

For this study, both the saturated and unsaturated soils must be considered. The unsaturated zone soils are important because uranium may still be bound in these soils. Consequently, the unsaturated zone is a potential continuing contaminant source to the groundwater. Uranium mobility in the saturated zone must also be included in the study, given the primary focus of the current remedial action, which is a pump-and-treat system.

## THE GEOCHEMICAL MODEL

Contaminant-soil interaction is generally described in terms of the following processes:
- Adsorption and desorption, including ion exchange;
- Precipitation and dissolution;
- Filtration and remobilization of colloids and suspended particles; and
- Diffusion into micro-pores.

For the majority of the site conditions, adsorption and desorption of the contaminant to the soil matrix are expected to dominate uranium transport [1]; therefore, the project was designed to understand controls on these processes. Precipitation and dissolution are also expected to influence uranium mobility near the source areas (i.e., the cribs) [1] and were investigated as well. The other processes listed were addressed to determine their relative importance to uranium mobility; however, they are not expected to be important to uranium mobility at the site.

An additional consideration for the model was the need to be able to predict uranium mobility for a range of geochemical conditions. Variable conditions are expected at the site due to the nature of the waste stream. Remedial options for the site may also require considering the effects of changing soil/groundwater chemistry, including pH, on uranium mobility. Empirically derived adsorption isotherm models cannot be used to extrapolate beyond the specific conditions used to develop the model.

Therefore, surface complexation adsorption models, which do allow extrapolation [2], were investigated for the project.

**Surface Complexation**

Surface complexation models are based on the chemical and physical properties of the soil, soil moisture (unsaturated zone), groundwater (saturated zone), and the waste stream characteristics.  Surface complexation models can be used to predict changes in adsorption as a function of pH and concentrations of competing ions and complexed species.  Therefore, surface complexation models are well suited to conditions of changing pH and soil/groundwater chemistry.

There are several surface complexation modeling schemes to choose from [2].  The models differ according to how the relationship between the sorbents and the sorbate is addressed.  The three most common types of surface complexation models are the diffuse layer model, the constant capacitance model, and the triple layer model.  Many researchers have noted that any of the surface complexation models do equally well at modeling and predicting the adsorption behavior of uranium and other metals accurately [3].  For this reason, and because it is the least complex of these models to parameterize and apply, the diffuse layer model was chosen for this study.

**SIGNIFICANCE OF $CO_2$ TO URANIUM MOBILITY IN THE VADOSE ZONE**

The concentration  of carbon dioxide ($CO_2$) in the soil gases can have a significant affect on uranium mobility for two reasons:
- Aqueous uranyl-carbonate complexes begin forming above a pH of about 5 or 6, which results in a more mobile form of uranium.  As the pH increases above approximately 8, uranyl-carbonates begin to precipitate.
- The uranyl ion ($UO_2^{+2}$) adsorption in soil is pH dependent and soil pH is strongly influenced by the concentration of $CO_2$ in the soil gas.  MSE's experiments show that uranyl adsorption by ferric oxides increases with a pH of up to 6 or 7, and then decreases with the uranium being desorbed, i.e., mobilized at higher pHs.

The mobility of uranyl [U(VI)] in unsaturated zone waters is influenced by the amount of carbonate present.  When U(VI) is in the form of a carbonate complex, it is poorly adsorbed and its minerals become orders of magnitude more soluble than if it occurs as an uncomplexed free $UO_2^{+2}$.  Important carbonate complexes include $UO_2CO_3^0$, $UO_2(CO_3)_2^{-2}$, and $UO_2(CO_3)_3^{-4}$.  The carbonate complexes dominate the chemistry of U(VI) in most natural waters above pH 5-6.  Their occurrence and abundance depend on both the pH and alkalinity of the water, as can be seen in the reaction forming the dicarbonate complex which may be written as:

$$UO_2^{2+} + 2HCO_3^- = UO_2(CO_3)_2^{2-} + 2H^+$$
(Eq. 1)

The equilibrium constant for this reaction is:

$$K_{eq} = \frac{\left[UO_2(CO_3)_2^{2-}\right] \cdot \left[H^+\right]^2}{\left[UO_2^{2+}\right] \cdot \left[HCO_3^-\right]^2}$$
(Eq. 2)

These expressions show that an increase in alkalinity ($HCO_3^-$) and/or pH favors formation of the complex. Currently, there is no cost-effective method to measure the pH of unsaturated zone moisture at depth. However, it is possible to extract unsaturated zone moisture and analyze it to determine the alkalinity. The pH of unsaturated zone waters depends on the $CO_2$ pressure in the unsaturated zone air, as is evident in the following reaction:

$$CO_2(g) + H_2O = 2H^+ + 2HCO_3^-$$
(Eq. 3)

For which:

$$K_{eq} = \frac{(P_{CO_2})}{[H^+]^2 [HCO_3^-]^2}$$
(Eq. 4)

The $CO_2$ pressure ($P_{CO2}$) of unsaturated zone air cannot be assumed equal to its value of about 0.0003 bars found in atmospheric air. Literature indicates that the concentration of $CO_2$ within the unsaturated zone is likely to be 10 to 100 times greater than the $CO_2$ concentration in the atmosphere above grade, where it occurs at the level of approximately 330 parts per million (ppm) [2]. Nevertheless, if the pressure of $CO_2$ gas in the unsaturated zone air and the alkalinity of the water are measured, the pH of soil moisture can be computed using:

$$\log P_{CO_2} = -pH + \log \frac{(\gamma_{HCO_3} mHCO_3^-)}{K_{CO_2} K_1}$$
(Eq. 5)

The log of the concentration of the $CO_2$ in the formation ($\log P_{CO2}$) is expressed as pressure. The soil-moisture ion-activity coefficient is denoted by $\gamma_{HCO3}$; and $m_{HCO3^-}$ is the soil moisture alkalinity, expressed as bicarbonate ($HCO_3^-$) concentration in moles/liter. $K_{CO2}$ is the equilibrium constant for $CO_2$ and carbonic acid ($H_2CO_3^-$); and $K_1$ is the equilibrium constant for $H_2CO_3$ and $HCO_3^-$.

The computed pH and measured alkalinity permit the calculation of concentrations of carbonate complexes using Equation 2, thereby making it possible to estimate the solubility of U(VI) and its tendency to be adsorbed. In other words, the measured alkalinity and $CO_2$ pressure permit estimating the mobility of uranium in the unsaturated zone, provided other geochemical information, e.g., sorption sites, etc., is available.

**UNSATURATED AND SATURATED ZONE CHARACTERIZATION**

In July 2001, borehole 299-W19-43 was drilled to a total depth of about 90-meters. The borehole was located approximately 250-meters southeast of the U-plant, near the intersection of Beloit Avenue and 16th Street (see Fig. 1). Split-spoon soil samples were recovered at various intervals as the borehole was advanced through the section. Stratigraphic and lithologic descriptions were recorded as the borehole was advanced to total depth. Three primary stratigraphic rock-units were described that included, from youngest to oldest, the Hanford formation, Plio-Pleistocene Unit, and Ringold Formation. Several subunits were recognized within each of the primary units. These units included Unit 1 and Unit 2 of the Hanford formation, Palouse Soil and Caliche of the Plio-Pleistocene Unit, and the Upper Ringold and Unit E Gravels of the Ringold Formation.

The split-spoon samples were used to characterize the physical and chemical properties of the soil and groundwater. The analysis of the soil chemistry and physical properties included identifying the major mineral composition; analysis of the grain coatings and precipitates present in the soil matrix; determination of the grain size distribution; and surface area of the sediments. The porewater analysis included determination of the major ions in solution, alkalinity, and pH. Dissolved $CO_2$ in the unsaturated zone waters was also estimated. This was done using $CO_2$ concentrations acquired via soil-gas sampling. $CO_2$ concentrations were measured at various intervals in the field from about 6- to 77-meters below ground surface (bgs).

## SORPTION SITE CHARACTERIZATION

A critical factor in developing a surface complexation model is the nature of the sorption sites contained in the soil. This includes understanding the sorption site chemistry, site density, and site structure. There are two general approaches to approximating the surface sites used for modeling sorption. These include the component additivity and generalized composite approaches [7]. The component additivity method is based on the cumulative sorption of a species by several different mineral phases present in the soils. In this approach, it is assumed that the wetted surface of the complex mineral assemblage is composed of a mixture of mineral phases whose surface properties are known from independent studies of the individual phases.

In the generalized composite approach, it is assumed that the surface composition of the mineral assemblage is inherently complex, and difficult to quantify in terms of the contributions of individual phases to adsorption. Instead, it is assumed that adsorptive reactivity of the surface can be described by surface complexation equilibria written with "generic" surface sites. The stoichiometric and equilibria constants are determined by fitting to experimental data. The generic surface sites used with the generalized composite approach is often approximated as an iron oxyhydroxide (the use of an iron oxyhydroxide is due to its relative abundance in natural soils) [7].

Davis et al. [7] compared the results of these two different approaches (i.e., generalized composite and component additivity) by modeling the sorption of zinc to a well-characterized aquifer material. They found that the generalized composite model required less information to implement and was more likely to be useful for immediate and practical applications; however, it may lead to an oversimplification of the problem. The component additivity approach may provide a more robust and transferable model; however, it requires that the mineral surface composition is well understood. Even with a thorough characterization of the mineral surfaces, some assumptions and parameter estimations may still be required for the component additivity model.

The primary sorbents of uranium found in naturally occurring geologic formations are iron and aluminum oxyhydroxides, clays, zeolites, phosphate minerals, and organic matter [2, 4, 5, 6]. The relative importance of these sorbents in a soil may be determined through physical and optical examinations, including particle size determinations, and chemical and mineralogical analysis.

Based on the work by Barnett [8], a citrate-bicarbonate-dithionite (CBD) extraction was performed on several soil samples from borehole 299-W19-43; and the amounts of extractable iron, aluminum, and manganese were determined for these soils. The CBD results showed that iron dominated the soils, yielding iron concentrations that were often two orders of magnitude greater than the aluminum and manganese (see Fig. 2).
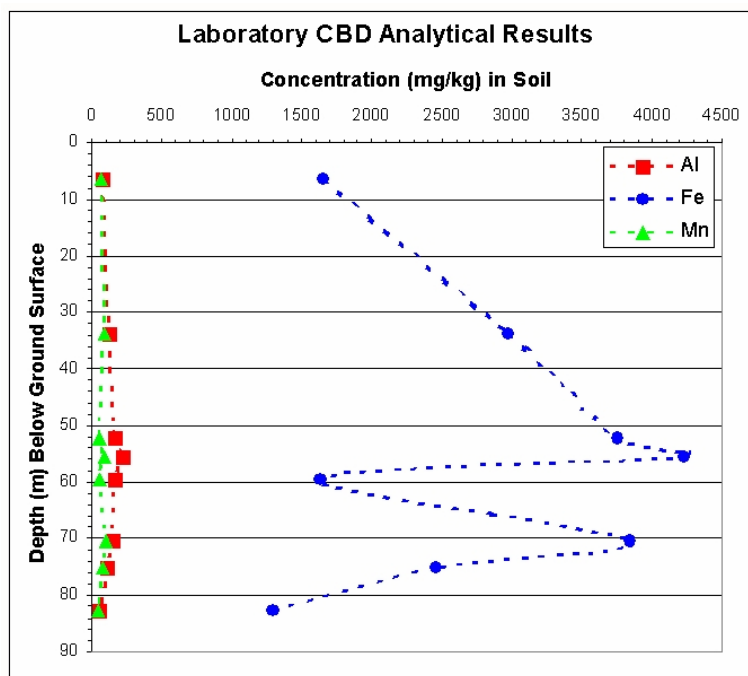
Fig. 2.   CBD extract results for Hanford soil samples from
borehole 299-W19-43

These results strongly suggest that for the soils from the 200 West Area of the Hanford site, iron is the dominant uranium sorbent.  As a result, the study focused on iron in the soils and its affect on uranium mobility.  Significant quantities of aluminum oxyhydroxides and other known uranium sorbents were not observed in the soils, and therefore were not considered for adsorption modeling.

The chemical composition of the soils was investigated using x-ray fluorescence and optical microscopy. The results indicated that iron was present in the soils as goethite, hematite, and magnetite.  This agreed with the significant amount of iron staining reported in the notes from the geologist logging the core during drilling of borehole 299-W19-43 (primary source of sample material for this project).

**Equilibrium Constants**

The model also requires equilibrium constants that describe the adsorption and desorption of protons, and important cations, ligands and metal complexes to the surface sites.  Measured and estimated intrinsic constants are available for a wide range of adsorption reactions on different mineral surfaces, as are other properties including mineral surface areas and surface charge densities [2,9].  It is important to note that many of these constants were determined under laboratory conditions and often may not apply to mineral phases found in nature, due to impurities in the natural mineral phases [8].

Regardless of the modeling approach, the equilibrium constants used by the model for sorption are often fit to measured sorption data [5,10].  The fitting is done using various parameter optimization or estimation routines.  Optimizing the parameters generally is required because the mineral phases in the soils are not pure forms as is typically studied in controlled laboratory experiments or because the actual amount of the sorbent is not adequately known.

**MODELING APPROACH**

Seven distinct geochemical units were identified for modeling using the soil, groundwater, and soil-gas characterization data,.  A simple component additivity model was then developed for each soil type.  These models accounted for the relative percentages of the different iron oxides (goethite, hematite, and magnetite) observed in the soils, as determined from optical microscopy combined with the iron extraction results for the soils. The geochemical model was generated in MINEQL+$^©$ v. 4.5, a Windows$^{TM}$ based chemical equilibrium modeling system that was derived from the public domain code, MINTEQA2.  Central to the geochemical model are the thermodynamic data and intrinsic constants that describe dissolution, precipitation, complexation, and adsorption of the modeled species.

Calibration of the geochemical model was completed through a series of laboratory batch tests to compare the measured sorption of U(VI) to the adsorption simulated by the geochemical model.  U(VI) surface complexation equilibrium constants for the geochemical model were adjusted within reasonable bounds in order to produce an acceptable correlation between the simulated and measured data.  After adjusting the uranyl surface complexation equilibrium constants for each soil type to fit the laboratory batch test data, a model of uranium sorption was produced for each of the soil types that could be used to simulate uranium sorption for varying conditions.  Model and laboratory results for the calibration work are shown in Fig. 3.
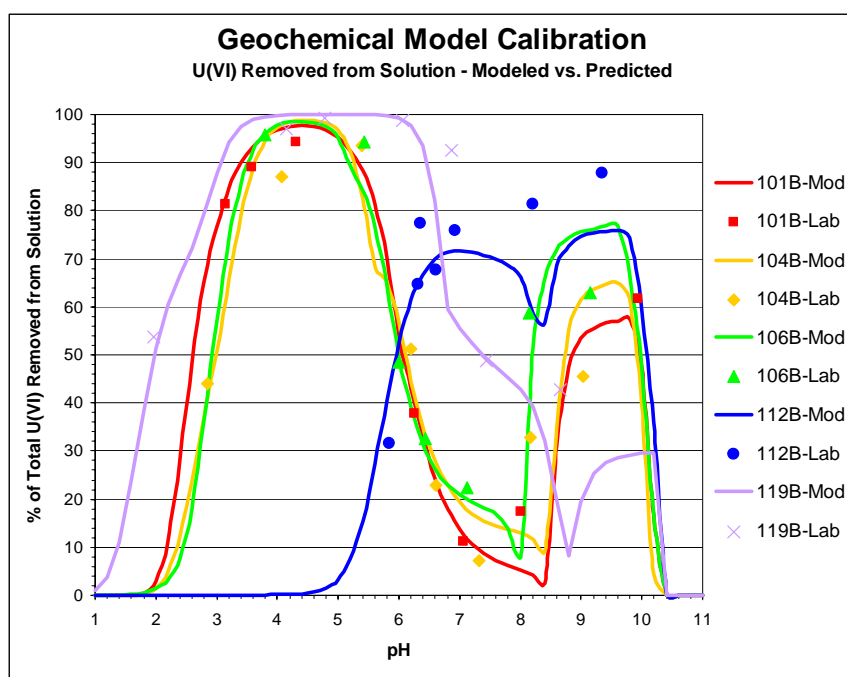


Fig. 3.  Modeled and laboratory results for geochemical model calibration

The geochemical model was validated in a similar manner.  Batch tests were performed on two additional soil samples.  U(VI) surface complexation equilibrium constants for the geochemical models were estimated according to the distribution of iron species.  The predicted results were compared to the measured results to validate that the model worked for additional soil and water chemistries. Model and laboratory results for the validation work are shown in Fig. 4.

**Geochemical Model Validation**

U(VI) Removed from Solution - Modeled vs. Predicted - "Initial" U Conc.
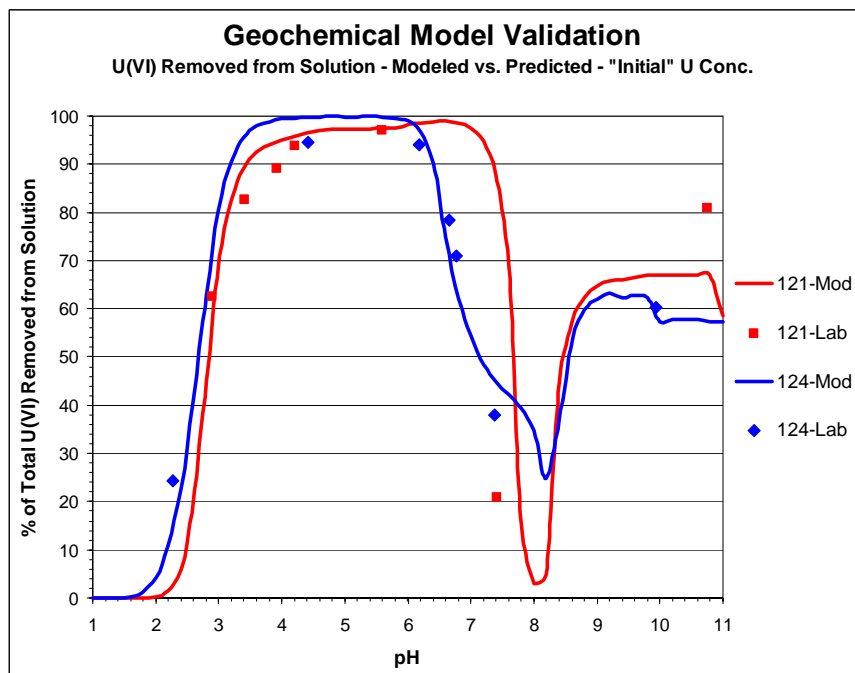
Fig. 4.  Modeled and laboratory results for geochemical model validation

In summary, the modeling approach used for this project combined the component additivity and generalized composite models.  The surface site concentrations were estimated from the discrete iron phases observed in the soil samples.  However, the equilibrium constants for sorption reactions were determined by fitting the model to the lab data, i.e., using a general composite approach.  The constants were then verified through comparison of further batch testing and modeling.

**ACKNOWLEDGEMENTS**

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