

ESTIMATING SITE CONCENTRATIONS IN SOILS FOR SURFACE COMPLEXATION MODELING OF SORPTION

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ABSTRACT

MSE Technology Applications, Inc. (MSE), in cooperation with Fluor Hanford, Inc. (FHI) is studying the partitioning of uranium between the soils and groundwater at the 200 West Area of the Hanford Site. The purpose of this effort is to produce an acceptable correlation between predicted and observed concentrations of uranium in the groundwater. The predicted uranium concentrations were derived through geochemical modeling of sorption using a surface complexation approach.

A surface complexation model often assumes a single, “generic” iron-hydroxide, with average sorption site properties for hydrous ferric oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), to be the primary sorbent. MSE found through citrate-bicarbonate-dithionite (CBD) selective extracts and optical microscopy that the iron-hydroxides in the Hanford soils consist of goethite ($\alpha\text{FeO} \cdot \text{OH}$), hematite (Fe_2O_3), and magnetite (Fe_3O_4). These iron species have sorption site properties (surface area and site density) that are significantly different than those of hydrous ferric oxide. MSE has derived a process of estimating sorption site properties for the given soil assemblage using individual sorption characteristics of those three minerals (goethite, hematite, and magnetite).

INTRODUCTION

MSE Technology Applications, Inc. (MSE), in cooperation with Fluor Hanford, Inc. (FHI), is studying the partitioning of uranium between the soils and groundwater at the 200 West Area of the Hanford Site. The purpose of this effort is to produce an acceptable correlation between predicted and observed concentrations of uranium in the groundwater. The predicted uranium concentrations were derived through geochemical modeling of sorption using a surface complexation approach. This information is used to estimate contaminant mobility, which is important in determining the risk factor imposed by the contaminant and subsequent remedial designs for the site. The application of surface complexation models for describing partitioning of contaminants between soil and groundwater is recognized as providing a more chemical and physical basis for the partitioning rather than simplifying partitioning by using partition coefficients obtained from empirical models based on a series of batch tests [1].

Development of a surface complexation model for a specific soil requires determining the type and concentration of sorption sites available to the contaminant(s) of interest. Such analyses often are carried out using microscopic methods (i.e., x-ray absorption fine-structure spectroscopy, scanning electron microscope, etc.); however, these can be costly to perform, may not be readily available, and/or are not always effective given the concentrations of sorption sites and/or contaminants that are present. An alternative approach for estimating the type and concentration of sorption sites is needed in order to advance the use of surface complexation

models for environmental site characterization and remediation. MSE used citrate-bicarbonate-dithionite (CBD) selective extract and optical microscopy methods to better estimate the type and concentration of sorption sites in soils from the 200 West Area of the Hanford Site, Washington.

SOIL, GROUNDWATER, AND SOIL GAS SAMPLING

Soil samples were obtained from borehole 299-W19-43 which was drilled to a depth of approximately 90-meters in the 200 West Area in the U-Plant Aggregate Area. Stratigraphic and lithologic descriptions were recorded and split-spoon soil samples were recovered at various intervals as the borehole was advanced to total depth. Three primary stratigraphic units were described. These 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 (sample 101B) and Unit 2 (samples 104B and 106B) of the Hanford Formation, Palouse Soil and Caliche (sample 112B) of the Plio-Pleistocene Unit, and the Upper Ringold (samples 119B and 121) and Unit E Gravels (sample 124) 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 CO₂ in the unsaturated zone waters was also determined using CO₂ concentrations measured via soil gas sampling. Concentrations of CO₂ were measured in the field at various intervals from about 6- to 77-meters below ground surface (bgs).

COMPONENT ADDITIVITY AND GENERAL COMPOSITE MODELING APPROACHES

There are two general approaches to approximating the surface sites used for modeling sorption. These include the component additivity and generalized composite approaches [8]. 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 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 properties 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, such as ferrihydrite (Fe₂O₃•H₂O). The use of an iron oxyhydroxide is due to its relative abundance in natural soils [2].

Davis et al. [3] 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.

MSE used a combination of the two approaches to characterize the sorption sites available in the Hanford soil samples. Following the component additivity approach, specific minerals, contributing to U(VI) adsorption, were identified; and the concentrations of sorption sites for each species were estimated. A total concentration of sorption sites was calculated according to the concentrations contributed by each sorbing mineral species, resulting in a single, “generic” sorption site. This is similar to the general composite model. MSE’s approach of creating a “generic” site that is based on the characterization of the individual sorption species provides a more refined estimate and understanding of the amount and nature of the sorption sites. **Fig. 1** diagrams the approach used by MSE to estimate the type and concentration of sorption sites in soils from the 200 West Area.

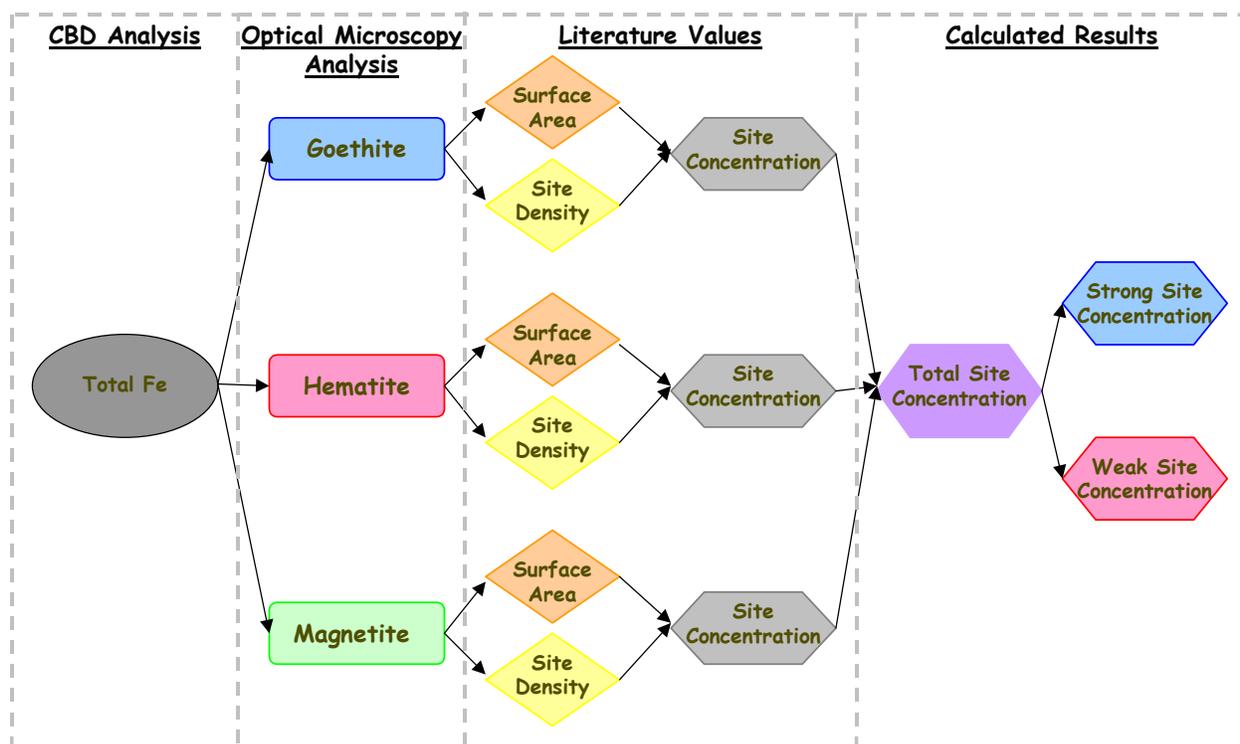


Fig. 1 MSE approach for estimating sorption site type and concentration

SORPTION SITE CHARACTERIZATION

Characterizing the nature of the sorption sites in the soil requires understanding the site chemistry, site density, and sorption site structure. Sorption of metal cations to solid surfaces has been investigated for many years. Much of this work is based on solid-solution interfacial chemistry [4]. Initially the work addressed sorption by pure mineral phases isolated in the laboratory, particularly iron mineral phases such as ferrihydrite, goethite, or hematite [5,6]. Recently, investigators have been developing surface complexation models to describe sorption by natural mineral assemblages such as those found in sands and clays. Many of these studies focused on Fe and Al oxyhydroxides as the primary sorbents due to their affinity for cation sorption and their relative abundance in nature.

The primary sorbents of uranium are iron and aluminum oxyhydroxides, clays, zeolites, phosphate minerals, and organic matter [5]. Studies by Barnett et al. have indicated that iron-hydroxide surface sites dominate U(VI) complexation in Hanford soils [2]. These studies also demonstrated that the surface complexation model developed by Waite et al. [7] for uranium sorption to ferrihydrite could be applied to the Hanford soils. The sorption sites were assumed similar to a ferrihydrite-like mineral phase, and the concentration of these sorption sites was estimated from the results of a citrate bicarbonate-dithionite (CBD) extraction, which is designed to extract the free iron oxides from the soils. Results suggested this approach gives a good first approximation for uranium sorption for the soils they used in their study.

All of the surface complexation models require the concentration of available sorbing sites in a given volume of the soil matrix as a primary input. This is a function of the surface area of sorbents exposed to the porewater solution and the surface charge (or site) density of the sorbents. The concentration of available sorbing sites is typically expressed as the number of moles of sorbing sites in contact with a liter of solution. The concentration of sorbing sites (Γ_{SOH}) is determined from the following relationship [5]:

$$\Gamma_{\text{SOH}}(\text{mol} \cdot \text{sites/L}) = \frac{N_{\text{S}}(\text{site/m}^2) \times S_{\text{A}}(\text{m}^2/\text{g}) \times C_{\text{S}}(\text{g/l})}{N_{\text{A}}(\text{sites/mole} \cdot \text{sites})} \quad (\text{Eq. 1})$$

where the concentration of sorbing surface sites is given in moles of sites exposed to a liter of solution, N_{S} is the surface site density, S_{A} is the surface area per weight of sorbent, C_{S} is the weight of sorbent in contact with a liter of solution, and N_{A} is Avogadro's number.

Citrate-Bicarbonate-Dithionite Selective Extracts

The chemical composition of the soils was investigated using x-ray fluorescence, which indicated that iron was present. This agrees with the significant amount of iron staining reported in the notes from the geologist logging the core during drilling of borehole 299-W19-43.

Based on the work by Barnett [2], a 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).

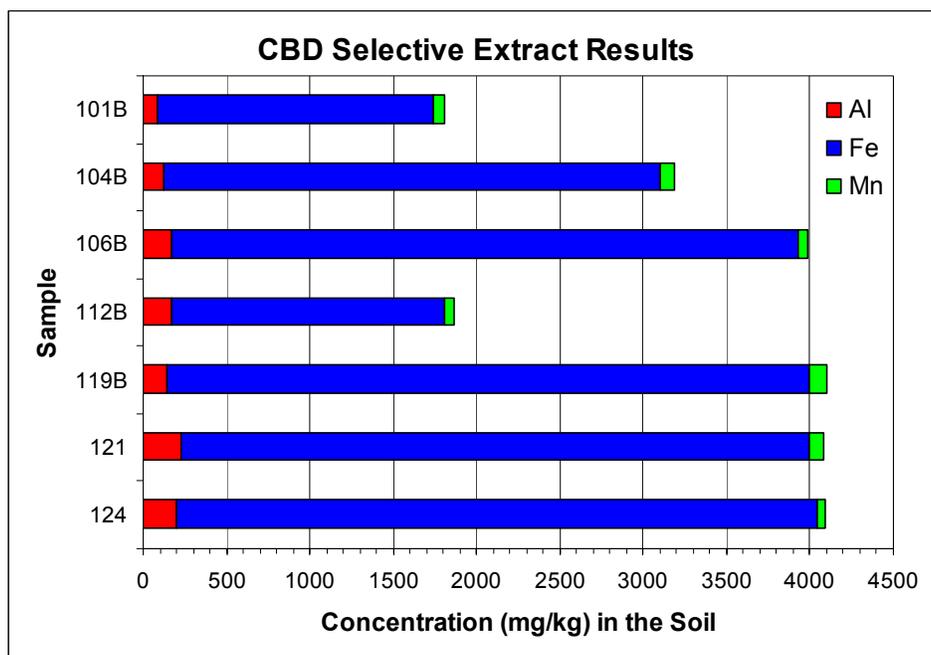


Fig. 2 Results of the CBD selective extracts performed on the Hanford soil samples

These results strongly suggest that for the soils from the 200 West Area of the Hanford site, iron is likely 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 hydroxides and other known uranium sorbents were not observed in the soils, and therefore were not considered for adsorption modeling.

Optical Microscopy

MSE initially modeled U(VI) adsorption for the Hanford soils by assuming all extractable iron was ferrihydrite. This followed the work performed by Barnett et al. [2]. Results showed that this modeling process over predicted uranium sorption. Consequently, MSE focused on identifying the specific iron species present in the soils.

Thin sections of the Hanford soil samples were made and optically examined with a petrographic microscope. MSE found that the iron in the Hanford soils was present in the form of goethite ($\alpha\text{FeO}\cdot\text{OH}$) or limonite ($\text{FeO}\cdot\text{OH}\cdot n\text{H}_2\text{O}$), hematite (Fe_2O_3), and magnetite (Fe_3O_4) or ilmenite (FeTiO_3). The percent relative abundances of these iron species are shown in Table I.

Table I Percent Relative Abundances of Iron Species in Hanford Soil Samples

Sample	Percent Relative Abundance of:		
	Goethite or Limonite	Hematite	Magnetite or Ilmenite
101B	16	10	74
104B	43	14	43
106B	25	50	25
112B	30	30	40
119B	84	11	5
121	23	3	74
124	27	4	68

The optical microscopy could not differentiate between goethite and limonite or magnetite and ilmenite. As a result, these two iron pairs are referred to as goethite and magnetite, respectively. Most significant is the fact that no ferrihydrite was identified in the soil samples. The iron species present in the Hanford soils (goethite, hematite, and magnetite) do not have similar sorbent site properties (i.e., surface area and site density) to ferrihydrite. As a result, assuming the total extractable iron determined through the CBD selective extracts is ferrihydrite is not valid for the Hanford soils examined.

Surface Area and Site Density

The number of sites contributed by each iron species depends on the surface area and site density of each iron species. A review of literature [5,8,9,10] showed that surface area and site density values significantly vary among iron species. Surface area and site density values for the iron species considered in this work are shown in **Table II**.

Table II. Surface Area and Site Density Values for Several Iron Species

Iron Mineral	Surface Area (m ² /g)	Site Density (sites/nm ²)
Goethite	45 – 169	2.6 – 18
Hematite	1.8 – 3.1*	5 – 22
Magnetite	5 – 25	2.31
Ferrihydrite	250 – 600	20
*1.8 m ² /g for natural hematite and 3.1 m ² /g for synthetic hematite		

As was previously mentioned, assuming the total extractable iron determined through the CBD selective extracts is ferrihydrite is not valid for the Hanford soils examined. As shows, this assumption leads to significantly higher total adsorption site estimations.

SORPTION SITE CONCENTRATIONS FOR HANFORD SOIL SAMPLES

Sorption site concentrations can be calculated using the data discussed above and Eq. 1 for the Hanford soil samples. **Table III** shows the calculated moles of goethite, hematite, magnetite, and total sites for the Hanford soil samples.

Table III. Calculated Moles of Sites for the Hanford Soil Samples

Sample	Moles of Sites Attributed to:			Total
	Goethite	Hematite	Magnetite	
101B	1.34×10^{-3}	1.09×10^{-5}	1.18×10^{-4}	1.47×10^{-3}
104B	6.47×10^{-3}	2.74×10^{-5}	1.23×10^{-4}	6.62×10^{-3}
106B	4.75×10^{-3}	1.24×10^{-4}	9.01×10^{-5}	4.96×10^{-3}
112B	2.49×10^{-3}	3.24×10^{-5}	6.29×10^{-5}	2.58×10^{-3}
119B	1.63×10^{-2}	2.78×10^{-5}	1.85×10^{-5}	1.64×10^{-3}
121	4.38×10^{-3}	7.43×10^{-6}	2.67×10^{-4}	4.65×10^{-2}
124	5.24×10^{-3}	1.01×10^{-5}	2.50×10^{-4}	5.50×10^{-3}

Surface areas used for goethite, hematite, and magnetite were 169, 1.8, and 25 m²/g, respectively, and, site densities used for goethite, hematite, and magnetite were 18, 22, and 2.31 sites/nm², respectively.

Had it been assumed that the iron in the soil samples was all ferrihydrite, the total moles of sites would have been much greater. Table IV compares the total moles of sites estimated using goethite, hematite, and magnetite to the total moles of sites computed using just ferrihydrite.

Table IV Total Moles of Sites Calculated from Goethite, Hematite, and Magnetite Compared to Total Moles of Sites Calculated Using Ferrihydrite

Sample	Total Moles of Sites Using:		$\frac{\text{Moles}_{(\text{Ferrihydrite})}}{\text{Moles}_{(\text{Goethite, Hematite, and Magnetite})}}$
	Goethite, Hematite, and Magnetite	Ferrihydrite	
101B	1.47×10^{-3}	3.31×10^{-2}	23
104B	6.62×10^{-3}	5.94×10^{-2}	9
106B	4.96×10^{-3}	7.49×10^{-2}	15
112B	2.58×10^{-3}	3.27×10^{-2}	13
119B	1.64×10^{-3}	7.67×10^{-2}	5
121	4.65×10^{-2}	7.51×10^{-2}	16
124	5.50×10^{-3}	7.65×10^{-2}	14

As Table IV shows, the total moles of sites calculated assuming the iron in the soil samples is ferrihydrite is 5 to 23 times greater than the total moles of sites calculated using goethite, hematite, and magnetite.

CONCLUSIONS

The concentration of sorption sites was estimated using results of the CBD and petrographic analyses and parameters describing the sorption site properties. Iron species can have significantly different sorption site properties (i.e., surface area and site density). Consequently, it is likely that the iron species do not equally contribute to the total concentration of sorption sites. Sorption site concentrations for specific iron species can be estimated from the surface area and surface site density defined for that iron species.

This approach to defining surface complexation model parameters results in a model that is based on the macroscopic properties of the soils and can be extrapolated over a broader area than those obtained from a limited number of discrete microscopic analyses. Thus, this approach is more applicable to site characterization and remediation as opposed to in-depth research aimed at understanding the microscopic mechanisms of sorption.

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