Development of a Geochemical Model for Uranium Transport in the Unsaturated and Saturated Sediments at the 200 West Area of the U.S. Department of Energy Hanford Site, Washington [MSE, ECCP-41]

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788

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3.24.2010
Date

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Background

"Development of a Geochemical Model for Uranium Transport in the Unsaturated and Saturated Sediments at the 200 West Area of the U.S. Department of Energy Hanford Site, Washington" (September, 2004) was prepared by MSE Technology Applications, Inc. This is the summary report for work conducted from 2001 through 2004. The work was funded by DOE Headquarters as FWP-HQ-LMT-02 under the Hanford Science and Technology Coordinating Group (STCG).

Supporting analytical work was conducted by PNNL, Lawrence Berkeley National Laboratory, and MSE.

The work was contracted to MSE through Bechtel Hanford Incorporated (BHI). The work was conducted under Scott W. Petersen, who accepted the deliverable from MSE. Dr. Peterson has retained the original single hardcopy of the text and plates. In January, 2010 electronic copies of the text (MS Word) and four plates (pdf) were obtained from MSE by Dr. Petersen.

The uranium 236 analyses were contracted to Lawrence Berkley by PNNL for MSE, but the results were not delivered until 2010. In January 2010, Jeff Serne of PNNL obtained the EXCEL file of uranium analyses from Lawrence Berkley. The U-236 isotope study is described in the text in section 6.2.

The report implements sampling and analyses that were formally planned by DOE/RL, the Washington Department of Ecology, BHI, CH2MHill Hanford Incorporated, and MSE data quality objectives document and the sampling and analysis plan.

Scot C. Adams

February 23, 2010

**DEVELOPMENT OF A GEOCHEMICAL
MODEL FOR URANIUM TRANSPORT IN
THE UNSATURATED AND SATURATED
SEDIMENTS AT THE 200 WEST AREA OF
THE U.S. DEPARTMENT OF ENERGY
HANFORD SITE, WASHINGTON**

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EXECUTIVE SUMMARY

MSE Technology Applications, Inc., (MSE) is funded by the U.S. Department of Energy Headquarters (DOE-HQ) under FWP-HQ-LMT-02 to contribute to fulfilling needs identified by the Hanford Science and Technology Coordination Group (STCG).

MSE focused the efforts of the work in the 200 West Area of the Hanford Site where a plume of uranium exists in the 200-UP-1 Groundwater Operable Unit. The objective of this project was to develop a conceptual model of uranium mobility that is controlled first by sorption processes in the unsaturated and saturated soils associated with the 216-U1/U2 Cribs in the 200 West Area of the Hanford Site. The primary task associated with this project was the geochemical modeling effort and it was the goal of this modeling effort to produce an acceptable correlation between predicted and observed concentrations of uranium in the groundwater.

The distribution of contaminants such as uranium in the soil profile depends on the physical properties of the waste stream, which provides the transport medium (i.e., water), and the chemical properties of the contaminant, which affect contaminant-soil interactions. Other characteristics affecting the contaminant soil interaction include the geologic and geochemical properties of the soil column and the composition of soil moisture and soil gases.

MSE chose to use a diffuse layer surface complexation model for the geochemical modeling efforts. The parameters required for the diffuse layer model include: the concentration of available sorbing sites in a given volume of the soil matrix; the surface area of the sorbents exposed to the groundwater; and the thermodynamic equilibrium constants for reactions involving the surface sites and aqueous components. The remaining parameters used in the geochemical modeling of UO_2^{+2} adsorption included aqueous component concentrations, CO_2 concentrations, and thermodynamic constants.

This report is a comprehensive report covering the work completed during the course of the project. The information included here was provided in "status reports", which were completed at the end of each fiscal year (FY) and is summarized below.

FY01 – The activities completed during FY01 include development of project planning documents, collection of soil and gas samples during installation of well 299-W19-43, and acquisition of borehole geophysical data from well 299-W19-43. The laboratory analysis of the samples obtained during the drilling was also initiated.

FY02 – The activities accomplished during FY02 include completing the laboratory analyses of the soil and soil gas samples obtained during the drilling of well 299-W19-43; reviewing information from previous reports and summarizing inventory of the wastes disposed of in the 216-U1/U2 Cribs; completing a sensitivity analysis of uranyl (UO_2^{+2}) adsorption; completing the initial laboratory batch testing for calibration of the geochemical model; and completing the first iteration of the geochemical model.

FY03 – The FY03 activities included analyzing of uranium isotope ratios for soil samples that were obtained from various boreholes surrounding the site, completing the geochemical model calibration, and validating the geochemical model.

FY04 – FY04 activities included performing chlorine (Cl) and sodium (Na) sensitivity analyses on the geochemical model; U-236 isotopic analyses performed on soil samples from the 200 West Area; and updating the current site conceptual model.

The results of the leach studies for all secondary contaminants indicate that untreated, spiked soil is not capable of meeting the regulatory limits for these contaminants at the levels added in the study. Treating spiked soil with only Ceramicrete appreciably reduced the leachability of selenium beyond that produced by the untreated soil, but did not significantly reduce the leachability of the other two secondary contaminants. The addition of sulfide in the form of sodium sulfide decreased the leachate concentration of selenous salt to near the regulatory limit from the treated soil. This sulfide addition also reduced the leachability of dichromate below the regulatory limit, but was not effective in reducing the leachate concentration of arsenic oxide.

A surrogate soil was identified with very similar properties to that of Oak Ridge soil that will allow field scale testing of placement techniques and methods at the MSE research and testing facility. The surrogate soil is from an inactive clay pit near Blossburg, Montana, approximately 60 miles from the MSE facility.

Cost estimates were prepared for two different Ceramicrete delivery techniques: deep soil mixing and jet grouting. Total remediation cost of the Building 81-10 area soils using Ceramicrete, with sodium sulfide as an additive, and deep soil mixing is estimate at \$5.4 million. Remediation using Ceramicrete with MBS as an additive, and deep soil mixing is estimated at \$6.0 million. Total estimated cost for Ceramicrete with sodium sulfide as an additive using jet grouting is \$7.1 million. Estimated remediation costs for Ceramicrete with MBS as an additive using jet-grouting technology is \$7.8 million. All cost estimates for soils remediation using ceramicrete showed significant cost savings compared to the \$27 million baseline remediation estimate for Building 81-10 soils.

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ACRONYMS AND ABBREVIATIONS

ACPC	Accelerated Cleanup: Paths to Closure
ARA	Applied Research Associates, Inc.
ASTM	American Standards of Testing and Materials
BET	Brunauer, Emmett, and Teller
BHI	Bechtel Hanford, Inc.
CBD	citrate-bicarbonate-dithionite
CHI	CH2M Hill Hanford, Inc.
CO ₂	carbon dioxide
Cps	counts per second
CPT	cone penetrometer test
DOE	U. S. Department of Energy
DOE-HQ	DOE Headquarters
DOE-RL	DOE-Richland
DOE-WETO	DOE-Western Environmental Technology Office
DOW	description of work
DQO	data quality objective
EGM	ethylene glycol monoethyl ether
EPA	Environmental Protection Agency
ERC	Environmental Restoration Contractor
ETF	Effluent Treatment Facility
FHI	Fluor Hanford Inc.
g	grams
km ²	square kilometers
ft bgs	feet below ground surface
FY	fiscal year
Kd	partitioning coefficient
kg	kilograms
L	liter
m	meter
MCL	maximum contaminant level
mg/L	milligrams per liter
mi ²	square miles
mL	milliliter
MOU	Memorandum of Understanding
MSE	MSE Technology Applications, Inc.
MTCA	Model Toxics Control Act
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
OU	operable unit
QAPP	quality assurance project plan
RAO	remedial action objective
RMSE	root mean squared error
ROD	Record of Decision
SAP	sampling and analysis plan
SCFA	Subsurface Containment Focus Area
SI	saturation index
SOH	strong sorption site
STCG	Science and Technology Coordination Group

ACRONYMS AND ABBREVIATIONS (CONT'D)

STR	Subcontractor Technical Representative
WHC	Westinghouse Hanford Company
WHO	weak sorption site
μg/L	micrograms per liter
UO ₂ ⁺²	uranyl
U(VI)	uranyl (alternate notation)
XRF	x-ray-florescence
XRD	x-ray diffraction

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1. INTRODUCTION

This year-end status report fulfills the fiscal year 2003 (FY03) Milestone M3-03 for Field Work Proposal FWP-HQ-LMT-02, "Task-A" "Subsurface Site Closure Planning and Longterm Monitoring, Subtask M". MSE Technology Applications, Inc. (MSE) is funded by the U.S. Department of Energy Head Quarters (DOE-HQ) under FWP-HQ-LMT-02 to contribute to needs at the Hanford Site related to uranium contamination in the subsurface, which is considered critical to the success of the Accelerated Cleanup: Paths to Closure (ACPC).

1.1 BACKGROUND

MSE is focusing the efforts of the work in the 200 West Area of the Hanford Site where a plume of uranium exists in the 200-UP-1 Groundwater Operable Unit. The contaminated groundwater is primarily associated with discharges to the U1 and U2 cribs in the 200 West Area. Currently, a pump-and-treat system is in place at the site that is 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. The purpose of the study is to focus on uranium and how it interacts with the soil in terms of adsorption to the soil matrix. Technetium-99, nitrate, and carbon tetrachloride are also present within the 200-UP-1 Groundwater Operable Unit in concentrations above the maximum contaminant level (MCL) for drinking water under the Safe Drinking Water Act. These contaminants were adequately addressed by the pump-and-treat system or are being addressed by other remedial systems and are not of specific concern at this site. However, other contaminants that may be present at the site may be considered from the standpoint of the impact they may have on the mobility of the uranium.

1.1.1 Previous Investigations

Previous investigations at the site include:

- U1/U2 Uranium Plume Characterization completed by Westinghouse Hanford Company (WHC), (WHC June 1, 1988);
- 200 West Area Limited Field Investigation by Bechtel Hanford, Inc., (BHI), (BHI, March 1995);
- Waste Site Grouping for 200 Areas Soil Investigations published by the DOE-Richland Office (DOE-RL), (DOE-RL, January 1, 1997); and
- 200 Areas Remedial Investigation/Feasibility Study (DOE-RL, April 1, 1999).

1.1.2 Remedial Action Objectives

The Remedial Action Objective (RAO) for uranium in the groundwater at the site, as stated in the Interim Action Record of Decision (ROD) for the 200-UP-1 Operable Unit (EPA, February 1997), is 480 micrograms per liter ($\mu\text{g/L}$). This value corresponds to 10 times the cleanup level for uranium under the Washington State Department of Ecology's Model Toxics Control Act (MTCA).

In FY99, the average uranium concentration in extraction well 299-W19-39 was 210 $\mu\text{g/L}$; uranium concentrations have ranged from 275 $\mu\text{g/L}$ in 1997 to 210 $\mu\text{g/L}$ at the end of FY99 in the extraction well. Downgradient, in well 299-W19-40, the uranium concentration was approximately 200 $\mu\text{g/L}$; however, concentrations of uranium within the plume exceed the RAO.

1.1.3 Conceptual Site Model

The following description of the distribution of uranium contamination at the site is taken from the Interim Action ROD for the 200-UP-1 Groundwater Operable Unit (EPA, February 1997).

The 200 West Area is an operational area of approximately 5.1 square kilometers (km²) [1.97 square miles (mi²)] where spent nuclear fuel was processed in four main facilities: U Plant (primarily uranium recovery); Z Plant (primarily plutonium separation and recovery); and S and T Plants (primarily uranium and plutonium separation from irradiated fuel rods).

Contamination in the 200-UP-1 Groundwater Operable Unit resulted from historic discharges of process water from the UO3 Plant to five primary liquid waste disposal sites (i.e., cribs). The predominant contaminants were uranium and technetium-99. The major portion of discharge to the soil column occurred between 1951 and 1968 via two cribs (216-U1 and 216-U2), which transported the mobile constituents, particularly technetium-99, to the water table. However, most of the uranium discharged to the cribs' was retained in the upper 20 meters (m) [66 feet (ft)] of the soil column. During the final years of the cribs operation (1966 through 1968), small volumes of highly acidic decontamination wastes were discharged, which resulted in the dissolution and transport of part of the previously deposited autunite (uranium phosphate). Low concentrations of uranium were detected in the groundwater monitoring wells near 216-U1/U2 during that period. The majority of dissolved uranium was distributed throughout the soil column beneath the cribs, with the largest concentration deposited above a caliche layer at about 50 m (164 ft) depth. During 1984, large volumes of cooling water were discharged to the adjacent 216-U16 crib, which reportedly resulted in the transport of uranium to the groundwater. This history and the contaminant flow path are captured in Figure 1-1, which was prepared by MSE to facilitate the understanding of the site.

During 1985, uranium concentrations in the groundwater abruptly increased from 166 to 72,000 pico Curies per liter (pCi/L). Limited pump-and-treat activities were initiated in 1985 to recover the uranium from the groundwater using ion exchange. During the 6 months of pump and treat, approximately 687 kilograms (Kg) [1,500 pounds (lbs)] of uranium were recovered and the concentration in well 199-W19-3 was reduced to 1,700 pCi/L.

From September 1995 to February 1997, the Phase I pump-and-treat injection operations used a single extraction well and a single injection well. Operations were halted from February 8, 1997, to March 30, 1997.

On February 25, 1997, an Interim Action ROD was issued for the 200-UP-1 pump-and-treat operations. The selected remedy consisted of pumping and treating the highest concentration zone of the uranium and technetium-99 plumes. Before the Interim Action ROD, groundwater was treated on site using ion-exchange technology and granular activated carbon. Since starting Phase II of the operations in March 1997, groundwater is transported to the Effluent Treatment Facility (ETF). Once treated, the groundwater is discharged to the state-approved land disposal site north of the 200 West Area.

In addition to the uranium and technetium-99 plumes, nitrate and carbon tetrachloride are also present within the 200-UP-1 Groundwater Operable Unit in concentrations above the MCL for drinking water. Nitrate contamination resulted from discharges of neutralized nitric acid to various cribs located in the U Plant and S Plant areas. The source for the carbon tetrachloride is believed to be upgradient and outside the 200-UP-1 Groundwater Operable Unit, and associated with the Z Plant disposal sites. The extent of

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200 West Area, Hanford Site**

- ① Dilute acidic liquid waste containing uranium was disposed to the ground through the 216-U1/U2 cribs from 1957 until 1968. The uranium was immobilized in the soil by the formation of an insoluble carbonate-phosphate compound.
- ② From 1966 through 1968, the pH of the waste stream decreased and the uranium was re-mobilized and deposited deeper into the soils, possibly to a caliche layer. The more acidic waste stream may have also altered the soils directly below the cribs.
- ③ In the early 1980's, cooling water was discharged to a crib (216-U16) located south of the 216-U1/U2 cribs, creating a perched water table on the caliche layer.
- ④ This perched water may have been responsible for transporting the more mobile uranium to a vertical conduit, such as a well or thin spot in the caliche layer.
- ⑤ Some of the uranium may have permeated to the soil below the caliche layer beneath the 216-U1/U2 cribs.
- ⑥ The mobile uranium traveled down the vertical conduit to the regional groundwater table. As it traveled, the uranium may have permeated into the soils surrounding the conduit.
- ⑦ Upon reaching the water table, the uranium spread out and formed the uranium plume found at the site.

Figure 1-1. Current conceptual model of uranium transport to groundwater.

carbon tetrachloride and nitrate contaminant plumes are much larger compared to uranium and technetium-99 plumes. Carbon tetrachloride contamination in the groundwater is found throughout the entire 200 West Area, as a small amount of carbon tetrachloride was used as a degreasing agent in the 200 Area. The nitrate plume extends from west of the 200 Area to the Columbia River and is much larger and coalesces with other nitrate contaminant plumes from a number of 200 West Area facilities.

The leading edge of the uranium plume has migrated beyond the 200 West Area boundaries. The combined uranium and technetium-99 plume covers an area of approximately 0.5 km² (0.2 mi²).

1.2 PROJECT OBJECTIVES

The objective of this project is to develop a conceptual model of uranium mobility, which is controlled first of all by sorption processes, in the unsaturated and saturated soils associated with the 216-U1/U2 cribs in the 200 West Area of the Hanford Site. The goal is to produce an acceptable correlation between predicted and observed concentrations of uranium in the groundwater. Contaminant mobility is defined as the rate the contaminant is transported in the subsurface and is controlled by sorption processes (sometimes simplified as retardation). Sorption is the partitioning of the contaminant between the soil and the groundwater and can be used to describe both adsorption and desorption.

1.3 SCOPE

The scope of the project includes the tasks given below.

- Sampling of the soil and porewater for analysis of chemical and physical properties to develop a surface complexation model describing uranium partitioning between the soil and the groundwater for the site.
- Using the surface complexation model to investigate the partitioning relationships that may exist for potential contaminant transport paths at the site.
- Simulating uranium transport for potential transport paths at the site, including its source.
- Updating the conceptual model of uranium transport at the site with the model, providing the best fit of the simulated results with observed data.

1.4 DATA SOURCES

The majority of the data that are being used for developing the geochemical model were obtained from analysis of soil and porewater samples acquired during the installation of well 299-W19-43 in FY01 within the UP-1 Operable Unit. Other data sources include soil samples from the Hanford core library, data obtained from a cone penetrometer test (CPT) conducted near the location of well 299-W19-43, and information obtained from previous documentation on the cribs of concern and their waste inventory.

The sampling effort, coordinated in conjunction with BHI, the organization responsible for work in this area before July 1, 2002, followed site work requirements and protocols. BHI, as representative of the host site, assumed responsibility for coordination of in-kind and direct sampling support for this effort and therefore provided the EM-40 cost sharing. The host site also provided support in the areas of site interface and documentation requirements.

1.5 PROJECT SCHEDULE

The project will be completed over a 4-year period. The sampling was completed, and the laboratory analysis was initiated during FY01. During FY02, the laboratory analyses and the stratigraphic, lithologic, and geochemical profiles for the site were completed. In addition, in FY02, the first iteration of a geochemical model and the laboratory batch tests for model calibration were completed. In FY03, the calibration of the geochemical model was completed and the model validated. In FY04, the conceptual model was refined. This status report was initially prepared at the end of FY01 and updated at the end of FY02, FY03, and FY04.

1.6 PROJECT PARTICIPANTS

The project participants have been MSE, BHI, Fluor Hanford Inc. (FHI), DOE-RL, and the Washington State Department of Ecology. The roles and responsibilities of each party are defined in the project management plan (MSE, 2001a) and the Memorandum of Understanding (MOU) (BHI, 2001a).

1.7 REPORT ORGANIZATION

This report is organized to capture the efforts completed during FY01, FY02, FY03, and FY04 and to provide sufficient background of the project to support these efforts. The report includes a summary of the project design and approach followed by a review of the activities completed during FY01, FY02, FY03, and FY04 and the results of these activities.

2. GEOCHEMICAL MODEL BASIS

The geochemical modeling approach to describe uranium mobility in the subsurface is based on the expected purpose or use of the model, which is to predict the partitioning of uranium between soils and groundwater under a range of conditions that may exist at the site. This approach determined the type of model [i.e., surface complexation verses empirically derived partitioning coefficient (K_d)] needed to meet the project objectives. The factors expected to play a key role in uranium mobility were identified through characterization of the soils from the site and a literature review. This information provided a basis for the model development.

2.1 THE GEOCHEMICAL MODEL

To describe the mobility of uranium in the subsurface, relevant geochemical and physical processes must be identified and understood. 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 micropores.

For the majority of the site conditions, adsorption and desorption of the contaminant to the soil matrix are expected to dominate uranium transport (EPA, 1999); therefore, the project has been 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) (EPA, 1999) and are being 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.

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. An additional consideration for the model is 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 (Langmuir, 1997), were investigated for the project. 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.

The results of sorption models, such as surface complexation models, are typically expressed as sorbate concentration in solution or the amount of sorbate adsorbed to a given surface area of soil material plotted against a parameter such as solution pH. Conversely, partitioning relationships that are very important for contaminant transport modeling can be derived by plotting the amount of sorbate in solution against the

amount sorbed to a weight of sorbent material (Langmuir, 1997; Pabalan et al., 1998). The power of the surface complexation approach is that the partitioning relationships can be developed for various soil conditions that currently exist at the site and for different conditions that might arise during remedial efforts. The result is a dynamic model for predicting uranium mobility at the site, which may then be used to:

- target the remedial action to the most probable subsurface region that has been the main contributor to the contaminant plume in the groundwater;
- select an appropriate remedial action to stabilize or remove the contaminant source; and
- evaluate options to meet the remedial action objectives for the uranium plume in the groundwater.

2.1.1 Surface Complexation Models

There are several surface complexation modeling schemes to choose from (Langmuir, 1997). The difference in the models reflects 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 (Turner, 1995). For this reason and because the diffuse-layer model is the simplest of these models to parameterize and apply, it has been chosen for this 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 sorbent surface area exposed to the porewater and the sorbent surface charge (or site) density. The concentration of available sorbing sites is typically expressed as the number of moles (mol) of sorbing sites in contact with a liter of solution. The concentration of sorbing sites (Γ_{SOH}) is determined from the following relationship (Langmuir, 1997):

$$\Gamma_{\text{SOH}} (\text{mol} \cdot \text{sites/L}) = \frac{N_s (\text{site/m}^2) \times S_A (\text{m}^2/\text{g}) \times C_s (\text{g/l})}{N_A (\text{sites/mole} \cdot \text{sites})} \quad (2-1)$$

In Equation 2-1, the concentration of sorbing surface sites is given in moles of monovalent sites exposed to a liter of solution. Additionally, 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 of sorbent sites per moles of sites. The primary sorbents of uranium found in naturally occurring geologic formations are iron and aluminum oxyhydroxides, clays, zeolites, phosphate minerals, and organic matter (e.g., Turner, 1994; Langmuir, 1997; Payne, 1999; and Giammar, 2001). 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.

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 (e.g., Dzombak & Morel, 1990; and Langmuir, 1997). 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 (Davis et al., 1998).

2.1.2 Sorption Site Models

A critical factor in developing a surface complexation model is the nature of the sorption sites contained in the soil. This includes understanding the site chemistry, site density, and sorption site structure. Soil scientists and geochemists have studied the sorption of metal cations to solid surfaces for many years (Dzombak & Morell, 1990), and much of this work is based on solid-solution interfacial chemistry (e.g., Stumm & Morgan, 1981). Initially the work addressed sorption by pure mineral phases isolated in a laboratory, particularly iron mineral phases such as ferrihydrite, goethite, or hematite (e.g., Langmuir, 1997, and Giammer, 2001).

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 iron and aluminum oxyhydroxides as the primary sorbents due to their affinity for cation sorption and their relative abundance. Examples of this work include the efforts by Davis and his colleagues who have worked extensively with zinc and lead sorption to sands from a Cape Cod aquifer (See Coston et al., 1995; Davis et al., 1998; Davis et al., 2001; and Kent et al., 2000) and Zachara and his colleagues who have worked on metal cation sorption by several different soils and mineral assemblages (see Cowan et al., 1992; Zachara et al., 1992; Zachara et al., 1994; Zachara et al., 1995; and Turner et al., 1996;).

In terms of uranium sorption, recent work by Barnett et al. (2002) demonstrated that the surface complexation model developed by Waite et al., (1994) for uranium sorption to ferrihydrite could be successfully applied to naturally occurring soils obtained at three different DOE sites, including the Hanford Site. 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. Their results suggested this approach gives a good first approximation for uranium sorption for the soils they used in their study.

There are two general approaches to approximating the surface sites used for modeling sorption, and these include the component additivity and generalized composite approaches (Davis et al., 1998). 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 one or more 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 are often approximated as iron oxyhydroxide as was done by Barnett (2002). The use of an iron oxyhydroxide when modeling sorption in soils is due to its relative abundance.

Davis et al. (1998) 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.

Regardless of the modeling approach, the equilibrium constants used by the model for sorption are often fit to measured sorption data (e.g., Zachara, Payne, Waite) with the fitting done using various parameter optimization or estimation routines. FITEQL (Herbelin & Westall, 1999) is a popular computer code used for geochemical parameter optimization. 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.

2.1.3 Significance of CO₂ to Uranium Mobility in the Vadose Zone

The concentration¹ of carbon dioxide (CO₂) in the soil gases has a significant affect on uranium mobility for two reasons: (1) aqueous uranyl-carbonate complexes begin forming above a pH of about 5 or 6, resulting in a mobile form of uranium, as the pH increases above approximately 8, uranyl-carbonates begin to precipitate; and (2) the uranyl ion (UO₂⁺²) adsorption in soil is pH dependent and soil pH is strongly influenced by the CO₂ concentration. 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 hexavalent uranium [U(VI)] in unsaturated zone waters usually depends on its occurrence as carbonate complexes, which make uranium highly mobile. 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 UO₂⁺². Important carbonate complexes include UO₂CO₃⁰, UO₂(CO₃)₂⁻², and UO₂(CO₃)₃⁻⁴. The carbonate complexes dominate the chemistry of U(VI) in most natural waters above pH 5 to 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:

The equilibrium constant for this reaction is:

$$K_{\text{eq}} = \left[\frac{(\text{UO}_2(\text{CO}_3)_2^{2-})(\text{H}^+)^2}{(\text{UO}_2^{2+})(\text{HCO}_3^-)^2} \right] \quad (2-3)$$

These expressions show that an increase in alkalinity and/or pH favors formation of the complex.

It is possible to extract unsaturated zone moisture and analyze it to determine the alkalinity; yet there is no cost-effective way to measure the pH unsaturated zone moisture at depth. However, the pH of unsaturated zone waters depends on the CO₂ pressure in the unsaturated zone air, as is evident in the following reaction:

For which:

¹ The concentration of a gas in a mixture of gas is equal to the partial pressure of the gas in the mixture with respect to the total gas pressure.

$$K_{eq} = \frac{(P_{CO_2})}{[H^+]^2 [HCO_3^-]^2} \quad (2-5)$$

The CO₂ pressure 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 CO₂ within the unsaturated zone is likely to be 10 to 100 times greater than the CO₂ concentration in the atmosphere above grade, where it occurs at the level of approximately 330 parts per million (ppm). Nevertheless, if the pressure of CO₂ gas in the unsaturated zone air and the alkalinity of the water are measured, the pH of soil moisture can be computed using Equation 2-6 (cf. Langmuir, 1997, p. 158):

$$\log P_{CO_2} = -pH + \log \frac{(\gamma_{HCO_3^-} m_{HCO_3^-})}{K_{CO_2} K_1} \quad (2-6)$$

In Equation 2-6, the log of the concentration of the CO₂ in the formation (logPCO₂) is expressed as pressure. The soil-moisture ion-activity coefficient is denoted by $\gamma_{HCO_3^-}$, and $m_{HCO_3^-}$ is the soil moisture alkalinity expressed as bicarbonate (HCO₃⁻) concentration in mol/L. K_{CO_2} is the equilibrium constant for CO₂ and carbonic acid (H₂CO₃), and K_1 is the equilibrium constant for H₂CO₃ and HCO₃⁻.

The computed pH and measured alkalinity permit the calculation of concentrations of carbonate complexes using Equation 2-3, thereby making it possible to estimate the solubility of U(VI) and its tendency to be adsorbed. In other words, the measured alkalinity and CO₂ pressure permit the estimation of the mobility of uranium in the unsaturated zone, provided other geochemical information (e.g., sorption sites, etc.) is available.

MSE proposed to focus soil-sampling activities in the Plio-Pleistocene unit, specifically the caliche layer often present in the unit, in an attempt to quantify the impact of the caliche layer on CO₂ concentrations in the formation air (MSE, 2001b). MSE also sampled the soil gases at depth and measured the CO₂ concentration in these gases. This effort was completed during the installation of the borehole and reported on in the FY01 status report.

2.2 MODELING APPROACH

The chemical composition of the soils was investigated using x-ray fluorescence (XRF) and optical microscopy, and the results indicated that iron was present in the soils as goethite, hematite, and magnetite. 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 (primary source of sample material for this project). An independent core logging effort by Mr. Bruce Bjornstad of Pacific Northwest National Laboratories (PNNL) also noted the presence of a significant amount of iron staining in the soils.

Following the work by Barnett et al., (2002), a CBD² 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. The soil characterization results are discussed in detail in the FY02 status report (MSE, 2002a). These results

² Typically, a CBD extraction will extract all of the free iron oxides while an acid ammonium oxalate (Tamm's reagent) will remove the amorphous iron oxide, which is the more reactive iron (Loeppert and Inskeep, 1988). However, the CBD was selected based on Barnett's work, which showed that it is an effective measure of the iron available for sorption.

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 has 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.

Using the soil, groundwater, and soil-gas characterization data, seven distinct geochemical units were identified for modeling. MSE initially applied the generalized component approach to modeling the uranium sorption for these soils by assuming all extractable iron was ferrihydrite as Barnett et al. (2002) had done but found that this model overpredicted uranium sorption.

A simple component additivity model was then developed for each soil type. These models accounted for the relative percentages of the different iron oxides observed in the soils, as determined from petrographic microscopy combined with the iron extraction results for the soils. 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 predict uranium sorption for varying conditions.

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 laboratory data (i.e., using a general composite approach).

2.3 SITE CONCEPTUAL MODELING ASSUMPTIONS

The modeling approach is primarily based on the assumption that the stratigraphy defined in nearby boreholes is locally consistent and representative of the project site. This assumes that the soils sampled during the well installation and samples taken from existing core(s) are representative of the condition of the soils below the cribs before the disposal of waste to the cribs.

An additional assumption made for the project is that the waste stream history is sufficiently well known such that when combined with the geochemical and conceptual models, the mass of uranium that is still being recharged to the groundwater from the soil column can be estimated.

3. FISCAL YEAR 2001 ACTIVITIES

The activities completed during FY01 are described in this section. These activities include development of project planning documents, installation of well 299-W19-43 from which soil and soil gas samples were obtained for analysis, acquisition of borehole geophysical data from well 299-W19-43, completion of an additional soil gas sampling using a CPT, and completion and submittal of an FY01 status report. The laboratory analysis of the samples obtained during the drilling was also initiated.

3.1 PLANNING DOCUMENT PREPARATION

Early in FY01, MSE and BHI worked together to better focus the project efforts and to plan the project objectives to meet the Hanford Site's need of quantifying the mobility of uranium in the unsaturated and saturated soils associated with the 216-U1/U2 Cribs in the 200 West Area. In addition to conference calls for the project coordination, several planning meetings were held at the Hanford Site, and the data quality objective (DQO) process was initiated to identify the project issues and focus the project goals. Representatives from MSE, BHI, the DOE Western Environmental Technology Office (DOE-WETO), DOE-RL, Washington State Department of Ecology, PNNL, and CH₂M Hill Hanford, Inc. (CHI) were involved in the initial project planning and DQO process.

From those initial planning meetings and the subsequent weekly conference calls, the planning documentation presented below was developed by MSE in support of the project.

- *Data Quality Objectives Summary Report for Development of a Conceptual Geochemical Model for Uranium Transport in the Unsaturated and Saturated Sediments at the 200 West Area of the DOE Hanford Site, Washington* (MSE, 2001c).
- *Multi-Year Implementation and Project Management Plan for Development of a Conceptual Geochemical Model for Uranium Transport in the Unsaturated and Saturated Sediments at the 200 West Area of the DOE Hanford Site, Washington* (MSE, 2001a).
- *Sampling and Analysis Plan for Development of a Conceptual Geochemical Model for Uranium Transport in the Unsaturated and Saturated Sediments at the 200 West Area of the DOE Hanford Site, Washington* [including the quality assurance project plan (QAPP)] (MSE, 2001b).
- *Memorandum of Understanding (MOU) Between MSE Technology Applications, Inc., and Bechtel Hanford, Inc. for Site Access and Quality Assurance, Environmental, Health, and Safety Oversight* (BHI, 2001a).
- *Health and Safety Plan for Carbon Dioxide Sampling of the Borehole at the 200 West Area of the Hanford Site in Support of the Uranium Mobility Study in the 200 West Area of the Hanford Site* (MSE, 2001d).
- *Description of Work: Soil Gas CO₂ Concentration and Soil Moisture Investigation at 200 West Area Hanford Site for the UP-1 Uranium Mobility Investigation* (MSE, 2001e).

Each of these documents was developed according to BHI requirements for conducting fieldwork on the Hanford Site and reviewed by BHI. DOE-RL and the Washington State Department of Ecology reviewed the DQO Summary Report, and the Sampling and Analysis Plan (SAP). DOE-RL also reviewed the Multi-Year Implementation and Project Management Plan and the Description of Work for the soil gas sampling. In addition to the preliminary planning meetings, MSE, BHI, and DOE-RL participated in

several supplementary meetings to further plan and finalize the field sampling efforts, field logistics, and support activities.

3.2 WELL 299-W19-43 DRILLING AND SAMPLING

To expedite the removal of uranium and technetium-99 from the groundwater in the 200-UP-1 Groundwater Operable Unit, DOE-RL and the Washington State Department of Ecology agreed to convert former injection well 299-W19-36 into an extraction well. Because of this action, a new groundwater monitoring well (299-W19-43) was needed in proximity to well 299-W19-36 to monitor extraction well performance, hydraulic conditions, and contaminant concentrations. Existing groundwater monitoring wells 299-W19-28, 299-W19-29, and 299-W19-34A were considered to meet this objective; however, wells 299-W19-28 and 299-W19-29 have recently gone dry, and well 299-W19-34A is screened too deep (top of screen is approximately 60 ft below the water table) in the aquifer to effectively monitor extraction well performance (BHI, 2001b).

Cable-tool drilling methods were used to advance borehole 299-W19-43 to a total depth of 296 ft from July 2, 2001, through July 20, 2001. The location of the borehole is shown in Figure 3-1. The installation and sampling of the well was completed by BHI. The sampling followed the MSE SAP (MSE, 2001b) prepared for the project.

Figure 3-1. Approximate location of well 299-W19-43 (from BHI, 2001b).

The borehole was advanced to 274.5 ft using a drive barrel and split-spoon sampling methods; a hard-tool bit was used to advance the borehole from 274.5 ft to total depth. Temporary threaded steel casing was used to keep the borehole open as the borehole was advanced to total depth. Twelve-inch-diameter casing was used to a depth of 50 ft; 8-inch-diameter casing was used to total depth. According to the project SAP (MSE, 2001b), split-spoon soil samples enclosed in Lexan liners were recovered at various intervals as the borehole was advanced through the section. The samples were submitted to Battelle Labs, the laboratory subcontracted by MSE for the laboratory analysis. In addition to the split-spoon samples, soil grab samples were collected at 10-ft intervals from cuttings for laboratory soil-moisture analysis. These were also submitted to Battelle Labs for analysis.

Stratigraphic and lithologic descriptions were recorded as the borehole was advanced to total depth. Three primary stratigraphic 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, and 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. A detailed stratigraphic column of these units was compiled and included all split-spoon sampling intervals, grab sample points, depths of temporary casing, and various geophysical logs.

3.2.1 Soil Chemical and Physical Properties

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 measurements for soil chemical and physical properties are listed in Table 3-1.

Table 3-1. Soil chemical and physical property measurements.

Parameter	Measurement Method	Reference
Sediment Mineralogy (to include grain coatings and precipitates)	Optical Mineralogical Analysis	Methods of Soil Analysis, Part I, Chapter 8
	X-Ray Analysis	Methods of Soil Analysis, Part I, Chapter 12
Shape Factor of Soil Particles	Optical Mineralogical Analysis	Methods of Soil Analysis, Part I, Chapter 8
Grain Size Distribution	Sieve Analysis	Methods of Soil Analysis, Part I, Chapter 15
Surface Area	BET ¹ Analysis	Methods of Soil Analysis, Part I, Chapter 16
Soil Organic Matter	Combustion	Methods of Soil Analysis, Part III, Chapter 34
Specific Density	Pycnometer Method	Methods of Soil Analysis, Part I, Chapter 14
Bulk Density	Core Method	Methods of Soil Analysis, Part I, Chapter 13
Speciation of Uranium Bound to Soil Matrix	Dissolution of Metals	Methods of Soil Analysis, Part III, Chapter 3
Identifying the Main Sorbent(s) of Uranium	Optical Mineralogical Analysis	Methods of Soil Analysis, Part I, Chapter 8
	Electron Microscope	NA
Surface Charge Density of the Main Sorbent(s) of Uranium.	Literature Values	Langmuir, 1997
Percent Soil Moisture (Field)	"Speedy" Soil Moisture	ASTM D 4944-89
Percent Soil Moisture (Lab)	Laboratory Measurement	ASTM D 4959-89 (1994)
Percent Soil Moisture (Borehole)	Neutron Moisture Log	ASTM D 5220-92

¹ BET = Brunauer, Emmett, and Teller

3.2.2 Groundwater Chemistry

The porewater analysis included determination of the major ions in solution, alkalinity, dissolved CO₂ in the unsaturated zone (via soil gas sampling), and pH. The measurements for porewater analysis are listed in Table 3-2.

Table 3-2. Porewater chemistry measurements.

Parameter	Measurement Method	Reference
Major Anions (SO ₄ , Cl)	Laboratory Analysis by Ion Chromatography	EPA SW-846, Method 9056
Total Recoverable Metals (Ca, Mg, Na, K)	Laboratory Analysis by Inductively Coupled Plasma Furnace	EPA SW-846, Preparation Method 3005A, ICP Method 6010B
Iron Speciation	Laboratory Analysis by Colorimetric	EPA Standard Methods 3500-Fe D
Speciation of Uranium	Laboratory Specific Analysis	NA
pH of Porewater-Vadose Zone	Computed from Alkalinity and Soil Gas CO ₂ pressure	
pH of Porewater-Saturated Zone	Electrometric Method	EPA SW-846, Method 9040B
Alkalinity (Forms) of Porewater	Titration	EPA Standard Method 2320B
Dissolved CO ₂ -Vadose Zone	Field Measurement of Partial Pressure of Soil Gasses	
Dissolved CO ₂ -Saturated Zone	Calculated from pH and Alkalinity	
Carbon Isotopic Compositions	Gas Chromatograph - Isotope Ratio Mass Spectrometry	

3.3 SOIL GAS INVESTIGATION

Dissolved CO₂ and alkalinity control the concentration of carbonate species, including uranyl carbonate complexes, in the porewater by affecting the pH of solution. Since it is not feasible to measure pH in the unsaturated zone porewater, dissolved CO₂ must be determined from measurements of the CO₂ concentration in the soil gas.

The investigation of CO₂ gas in the unsaturated zone consisted of field measurements of CO₂ concentration, analytical confirmatory work on CO₂ concentration, and isotope composition. Field measurements were completed for depths from 80 to 253 feet below ground surface (ft bgs) while drilling using a cable-tool drilling rig. The soil-gas sampling intervals are described in Table 3-3.

Soil-gas samples were submitted to the University of Waterloo Environmental Isotope Laboratory, also working under subcontract to MSE, for analysis. However, the sampling containers were inappropriate for the length of time the samples were held by the laboratory, which compromised the quality of the analytical results. The CO₂ investigation on the upper section of the unsaturated zone (ground surface to 43 ft-bgs) was completed using a cone penetrometer; the intervals sampled are described in Section 3.3.1, Summary of CPT Soil Gas Sampling.

To enable the collection of this data, MSE developed the "Subsurface CO₂ Sampling System," which was subsequently used to collect the soil-gas data during the borehole drilling. Because of MSE's use of this innovative system at the Hanford Site, DOE-RL was able to claim an additional deployment during FY01.

Table 3-3. Soil gas sample intervals.

Sampling Depth (Ft)	Rock Unit	General Lithology
80	Hanford – Unit 2	Medium to Coarse Sand
135	Hanford – Unit 2	Fine Sand
170	Hanford – Unit 2	Sandy Silt
194	Caliche	Calcareous Silty Sand
207	Upper Ringold	Silt
217	Upper Ringold	Sandy Silt
228	Upper Ringold	Sandy Silt
253	Unit E Gravels	Sandy Gravel

3.3.1 Summary of CPT Soil Gas Sampling

MSE subcontracted Applied Research Associates, Inc. (ARA) to provide CPT support for soil gas sampling and additional data acquisition in the 200 UP-1 Groundwater Operable Unit at the 200 West Area of the Hanford Site. The scope of work was to acquire data (i.e., soil gas samples, pore pressure, conductivity (for soil moisture estimation), sleeve friction, and tip stress) from the surface to at least 100 ft bgs in the area near well 299-W19-43. Up to three boreholes were planned for acquiring the CPT data. In the end, however, the CPT was not able to achieve the 100 ft performance depth.

Three borehole locations were positioned 15 ft to the south of well 299-W19-43 and 10 ft apart, as described in the Description of Work for this activity prepared by MSE (MSE, 2001e). The CPT tools consisted of a cone “sipper” and the basic tool head for acquiring pore pressure, conductivity (soil moisture), sleeve friction, and tip stress. For the first borehole, soil-gas samples were acquired every 5 ft starting 5 ft bgs and continuing down to a depth of approximately 43 ft bgs, the depth achieved before refusal. While tripping out of the hole, the cone “sipper” and one length of rod were lost at approximately 8 ft bgs. After attempts to recover the equipment failed, ARA pushed to a depth of 40.8 ft bgs and backfilled with bentonite granules to a depth of approximately 10 ft bgs.

At the second borehole location, ARA set up the basic CPT tool head for acquiring pore pressure, conductivity, sleeve friction, and tip stress. ARA pushed the basic tool head to a depth of 63.5 ft bgs before meeting with refusal. Like the previous push, resistance was encountered at about 41 ft bgs. The second hole was backfilled with bentonite granules to a depth of approximately 8.5 ft bgs.

Instead of moving to the third borehole location, ARA attempted another push at the second borehole location, approximately 2 ft from the first attempt. This time the cone “sipper” was used. Unfortunately, ARA was only able to push down to 42.41 ft bgs before meeting refusal. During the push, MSE acquired soil gas samples at 20, 40, and 42.41 ft bgs. This hole was backfilled with bentonite granules to a depth of approximately 8.5 ft bgs.

It was decided that additional pushes would most likely have similar results. Consequently, the remaining upper portions of the boreholes were abandoned with cement and tagged as per the MSE Subcontract Technical Representative’s (STR) request.

3.4 GEOPHYSICAL BOREHOLE LOGGING

To complement the geologist's observations and the analytical laboratory's data, high-resolution spectral gamma and neutron moisture data were acquired from 50 to 257 ft bgs in well 299-W19-43. The purpose for these data was to better define the distributions of the soil moisture and gamma-emitting isotopes between the soil sample intervals.

The results of the logging effort are presented and discussed further in the FY02 status report (MSE, 2002a). Under subcontract to MSE, Duratek completed the logging efforts during off-hours to prevent interference with drilling activities.

The spectral gamma logging was completed using standard logging procedures including those described in American Society for Testing and Materials (ASTM) D 5753-95e1 and ASTM D 6274-98 (total gamma). Data acquisition was completed in a continuous logging mode at a rate that ensured the data are valid on an interval of at least 1 ft. The standard energy windows for potassium, uranium, and thorium were recorded and plotted. Other gamma-emitting isotopes of interest that were also addressed by the spectral gamma logging are shown in Table 3-4. The logging report from Duratek is included in Appendix A.

Table 3-4. Gamma-emitting isotopes in addition to K, U, and Th isotopes.

Cs-137	Co-60	Pu-238	Pu-239	Pu-240
Eu-152	Eu-154	Eu-155	Ra-226	Ra-228
Na-22	Tc-99	Th-228	Th-232	U-233
U-234	U-235	U-238		

Neutron soil-moisture logging was completed using standard logging procedures, including those described in ASTM D 5753-95e1. Data acquisition was completed in a continuous logging mode following the procedures outlined in Sections 8.2 through 8.4 of ASTM D 6031-96. The logging proceeded at a rate that ensured the data are valid on an interval of at least 1 ft. The 8-inch Duratek calibration coefficients were used for the soil-moisture logs as described in the moisture log analysis and summary provided by Duratek for this effort. A copy of the summary is included in the FY02 status report (MSE, 2002a).

4. FISCAL YEAR 2002 ACTIVITIES

The activities accomplished during FY02 are described in this section. These activities include:

- completing the laboratory analyses of the soil and soil gas samples obtained during the drilling of well 299-W19-43;
- reviewing information from previous reports and summarizing inventory of the wastes disposed of in the 216-U1/U2 Cribs;
- incorporating/updating the data and information from the geologic logging, soil moisture testing, geophysical measurements, hydrogeologic information, and the analyses of the soil and soil gas samples collected from the borehole into the geochemical model;
- evaluating the processes and geochemical reactions that are important to the mobility of uranium within the unsaturated and saturated soils;
- completing the work plans for the calibration and validation of the geochemical model;
- completing the first iteration of the geochemical model;
- completing the initial laboratory batch testing for calibration of the geochemical model;
- initiating the procurements to support the validation tasks; and
- completing and submitting the FY02 status report.

4.1 LABORATORY AND FIELD MEASUREMENTS

The analyses of the laboratory studies of the soil, soil moisture, and gas samples obtained from the borehole drilled in the 200 West Area were completed. Petrographic studies of thin sections made from the soil samples were also completed. In addition, the CO₂ data from the soil-gas field studies were analyzed as they pertain to the formation moisture pH (MSE, 2002a). Additionally, the stratigraphic columns showing the results of the sampling and analysis originally prepared in FY01 were updated to reflect the new information that had been acquired during FY02. These stratigraphic columns were included in the FY02 status report and referenced as data plates. All of the data plates have the stratigraphic units, graphic lithologic log, and geologist's observations included for reference and continuity between each plate.

Data and information from the geologic logging, soil moisture testing, borehole geophysical measurements, hydrogeologic information, and analyses of the soils and gas samples collected from the borehole were incorporated into the geochemical model. The information obtained from the data was used to evaluate the processes and recognize geochemical reactions that are important to the mobility of uranium within the unsaturated and saturated soils associated with the groundwater contamination from the 216-U1/U2 Cribs in the 200 West Area at the Hanford Site.

4.1.1 Field Observations of Lithology

Generally, the lithology of the section consists of sands, gravels, silts, and calcareous dominated deposits. Saturated sediments were found to occur 257 ft bgs. A detailed lithologic description is presented for each major stratigraphic unit and subunit. Additionally, these observations are presented graphically on Plate 1.

4.1.1.1 Hanford Formation

The Hanford formation near 299-W19-43 is approximately 181 feet in thickness and consists of two units of unconsolidated sediments (Unit 1 and Unit 2) that make up the primary thickness of the vadose zone. Unit 1 is approximately 67 ft thick and Unit 2 is approximately 114 ft thick.

4.1.1.1.1 Hanford Unit 1

Unit 1 extends from the ground surface to approximately 67 ft bgs. Sediments of the Hanford formation are generally coarser grained than underlying sediments of Unit 2 and consist generally of a series of unconsolidated fining-upward sequences of gravels, sands, and silts.

This unit is a highly permeable facies that varies between very fine to coarse-grained sands, silty sands (generally very fine to medium grained), gravelly sand (fine to coarse grained sands), and minor interbeds of silt. Generally, the sand fraction consists of grains that range between 50 percent to 70 percent basalt and 30 percent to 50 percent felsics (quartz and feldspars) with trace muscovite and biotite. Gravels are generally basaltic (fine to coarse gravels with rare cobbles to 4 inches in diameter) and occasionally coated with a variable coating of calcium carbonate. Subsurface moisture was described in the field as dry to damp. Damp sediments were generally found to be associated with the finer grained material (silts). A weak to strong reaction with hydrochloric acid (1 Normal) began in sediments eight feet below existing grade and continued through the unit. This indicates that the sands and silts have variable amount of calcium carbonate cement within the matrix. Sands are especially calcareous near 52 feet, 54 feet, and 58 feet below existing grade. Oxides of iron often stain mafic minerals (e.g., biotite); partings associated with interlaminated silts and fine sands are commonly stained, especially near 29 feet below existing grade.

Three split-spoon samples and nine grab samples were recovered from Unit 1. These included two split-spoon samples (MSE core samples 101 and 102) and one split-spoon sample recovered for Bechtel Hanford for waste designation. Nine grab samples were collected to quart-size tins to determine moisture content.

4.1.1.1.2 Hanford Unit 2

Unit 2 of the Hanford formation extends from 67 ft bgs to 181 ft bgs. Sediments of the Hanford Unit 2 formation are generally finer grained than overlying sediments of Unit 1 and consist typically of interstratified sands and silts that make up a series of fining-upward sequences. Unit 2 sediments become more silty and clayey toward the base of the unit. There is an unconformity between this unit and the underlying Plio-Pleistocene Unit.

The Hanford Unit 2 consists of a sequence of fine to coarse-grained sands with interstratified silty sands and silt that occurs below a gravelly sand (medium to coarse grained) associated with the base of Unit 1. Sands immediately below the base of Unit 1 are similar to those described in Unit 1 and consist of approximately 70 percent basalt and 30 percent felsics. These sands become more felsic with depth and generally contain 25 percent basalt and 75 percent felsics near 159 feet and 90 percent felsics by 161 feet. Generally, sediments of Unit 2 become damp below 70 feet. Sands, interbedded silts and clays below 155 feet become slightly more calcareous and exhibit a strong reaction with hydrochloric acid compared to sediments stratigraphically above. However, scattered carbonate nodules and accretions were observed near 68 feet and strong reactions with hydrochloric acid were observed between 77 feet and 80 feet. Scattered and infrequent gravels associated with a medium to coarse-grained sand near 70 feet are partially coated with carbonate-rich clay. A clastic dike was observed between 159 feet and 161 feet. This sedimentary feature consisted of calcareous medium sand penetrating a plastic clay. Iron oxide stains and alteration of mafics are rare and were observed in a sand interval between 156 feet and 159 feet.

Unit 2 becomes clayey and silty with interbeds of very fine sand near 168 feet. This lithology is often laminated and becomes calcareous near 180 feet with calcareous accretions or possibly calcareous rip-up clasts associated with the contact of the underlying Plio-Pleistocene Unit. Severe iron-oxide alteration

observed in silts near 182 feet associated with laminations and partings. Unit 2 forms an unconformable and erosional contact with the underlying Plio-Pleistocene Unit. This contact occurs near 181 feet. Four split-spoon samples (MSE core samples 103 through 106) and eleven grab samples (quart-size tins for moisture) were recovered from Unit 2.

4.1.1.2 Plio-Pleistocene Unit

The Plio-Pleistocene Unit near 299-W19-43 is approximately 24.4 feet in thickness, extending from 181 ft bgs to 205.4 ft bgs. It consists of two subunits: Palouse Soils and Caliche.

4.1.1.2.1 *Palouse Soil*

Palouse Soil extends from 181 ft bgs to 186 ft-bgs. The sediments consist of dry to damp calcareous silts that are well laminated and have a moderate to strong reaction with hydrochloric acid. This unit contains approximately 10 percent to 15 percent fine sand, 80 percent silt, and 5 percent clay. Occasional iron-oxide stringers and stain along partings and possible root traces were observed. These silts are five feet in thickness and grade to a silty and gravelly very fine to coarse-grained calcareous sand near 186 feet (top of Caliche).

A single split-spoon sample was recovered from the Palouse Soil (MSE Core Sample 107).

4.1.1.2.2 *Caliche*

Silty and gravelly calcareous sand was picked as the top of the Caliche near 186 ft bgs and extends to a depth of 205.4 ft bgs. This sand (very fine to coarse grained that includes 15 percent fine to coarse gravels and 15 percent silt) is well cemented with calcium carbonate from 186 ft bgs 196 ft bgs. These sands are commonly stained with oxides of iron and alteration to clay is throughout the matrix and grade into calcareous silty sands near 196 feet with common calcium carbonate nodules and stringers.

Dry to slightly moist calcareous silty sands make up the primary thickness of the Caliche Unit and occur between 196 feet and 205.4 feet. Calcareous stringers and accretions are common in this unit that consists of approximately 80 percent fine to medium sand and 20 percent silt. Calcium carbonate cemented root casts are common between 201 feet and 202 feet. Basalt content of sand fraction ranges from 25% to 45% with the balance composed primarily of quartz. These silty sands become less calcareous toward the contact with the underlying Upper Ringold near 205.4 feet where they grade to weakly laminated silt. Laminar partings are coated with calcium carbonate near the contact with the Upper Ringold Formation and calcium carbonate nodules are common near the contact. Non-calcareous stringers (possibly gypsum) occur in these silty sands near 204 feet. These silty and calcareous sands form an unconformable contact with the underlying silts of the Upper Ringold Formation that occurs near 205.4 feet.

Nine split-spoon samples were recovered from the Caliche Unit (MSE Core Samples 108 through 116).

4.1.1.3 Ringold Formation

Two units of the Ringold Formation were recognized and described as borehole 299-W19-43 was advanced. These units included the silts and silty sands of the Upper Ringold and sandy gravel of the Unit E Gravels. Approximately 90 feet of Ringold sediments were described between 205.4 feet and total depth (295.72 feet).

4.1.1.3.1 Upper Ringold

Upper Ringold extends from 205.4 ft bgs to 251.5 ft bgs. The sediments in the Upper Ringold consist of 46.1 feet (205.4 feet to 251.5 feet) of silt, sandy silt, and silty sand (236.5 feet to 251.5 feet). Laminated and damp calcareous silt occurs near 208 feet with infrequent oxides of manganese visible along partings; carbonate content, associated with partings, rapidly decreases below 210 feet. The unit is bioturbated near 209 feet (calcium carbonate filled burrow) and grades to sandy silt near 219 feet with common stains of iron oxides and scattered carbonate-rich accretions near 214 feet and 216 feet. Convoluted silty clay occurs near 223 feet that grades into sandy silt near 225 feet and silty sand near 237 feet and becomes less calcareous below 210 feet. No reaction with hydrochloric acid near 230 feet. Silty sand is the dominant lithology from 237 feet to 251.5 feet. This sand is very fine to medium grained (10 percent basalt grains and 90 percent felsics) with about 20 to 40 percent silt and has no reaction with hydrochloric acid. Trace amounts of muscovite and chloritized biotite are present. Sand fraction increases to approximately 95 percent near 243 feet and becomes very fine to fine grained with approximately 5 percent silt. Unit becomes slightly moist near 250 feet.

Five split-spoon samples were recovered from the Upper Ringold (MSE Core Samples (117 through 121) and five grab samples (quart-size tins) were recovered to be analyzed for moisture.

4.1.1.3.2 Unit E Gravels

Unit E Gravels consist of sandy gravel and silty sandy gravels from 251.5 feet to total depth of borehole 299-W19-43. This unit becomes saturated near 257 feet.

Gravels consist of fine to coarse with minor amount to 4-inches in diameter. Gravel ranges from 50 percent near 252 feet and increases to approximately 65 percent by 255 feet. Gravels are dominantly quartzites and meta-igneous. Silt increases from five percent near 252 feet to approximately 10 percent near 255 feet and 15 percent near 268 feet. Sand content decreases from 45 percent near 252 feet to 25 percent near 255 feet. Sand fraction is fine to coarse grained (60 percent to 80 percent fine to medium) and consists of 5 percent to 10 percent basalt grains and 90 percent to 95 percent felsics with trace muscovite. No reaction with hydrochloric acid observed.

Gravels commonly coated with fines that include blackish-gray oxides of manganese and iron-oxide stains (reddish-orange). Intergranular filling also includes flecks and blebs of non-calcareous material (possibly calcium sulfate, similar in appearance and color to calcium carbonate but no reaction with hydrochloric acid observed) and small sooty (blackish-gray) nodules likely rich in oxides of manganese. Slight chloritization of mafics occurs between 260 feet and 270 feet.

Three split-spoon samples were recovered from the Upper Ringold (MSE Core Samples (122 through 124) and one grab sample (quart-size tin) was recovered to be analyzed for moisture.

4.1.2 Geophysical Logging Data

The results of geophysical logging are discussed in this section. The logs acquired include natural gamma, spectral gamma, and neutron soil moisture. The natural gamma log is presented graphically on Plate 1; the spectral gamma logs are shown on Plate 2, and the neutron soil-moisture log is presented on Plate 3. The logs were placed on the data plates that contain information similar or relevant to the type of information contained in the individual geophysical logs. For example, the spectral gamma logs are shown with the XRF data. This allows for a comparison between the results and can be used as a means of cross checking.

Some general observations on the response of the logs to observations made during drilling are presented followed by specific discussions of select intervals. Because the geophysical logs begin at 50 ft-bgs and continue to the water table (257 ft bgs), the observations of the log responses do not include the near surface portion of the well (0 to 50 ft-bgs).

The geophysical logging report completed by the subcontractor (Duratek) is included in Appendix A.

4.1.2.1 General Geophysical Log Observations

A comparison of the geophysical logs to the lithologic log for well 299-W19-43 indicates the neutron soil moisture and natural gamma data are good indicators of grain size. Finer grained materials tend to retain more moisture than coarse grained materials, resulting in the positive neutron soil-moisture response in these intervals. Additionally, the finer grained sediments generally have silts and some clay minerals. These tend to be composed of the more felsic minerals, which contain potassium, some of it in the form of potassium-40, the most dominant naturally occurring gamma emitting isotope found in nature.

An example of the relationship between the neutron soil-moisture data, the natural gamma data, and the fine-grained materials noted on the lithologic log is observed from 50 to 53 ft-bgs. In this interval, fine sands interbedded with silt were observed during drilling. These zones of interbedded silt exhibit increased soil moisture and increased natural gamma activity.

A second example of the relationship between the neutron soil moisture data, the natural gamma data and the observed lithology can be seen in the interval from 58 to 64 ft-bgs. This interval was described as sand with coarse gravels. The neutron log indicates that no significant soil moisture exists in this interval and the natural gamma count decreases noticeably in this interval.

A general observation with respect to the natural gamma activity is related to the source of the gamma emissions as observed from the spectral gamma data on Plate 2. The natural gamma count appears to be primarily a function of the potassium-40 in the sediments, which typically is around 15 pCi/g for these sediments. The potassium-40 spectral gamma data for correlates well with the x-ray-fluorescence (XRF) data for potassium as shown on Plate 2. *[Note, the XRF data, which are discussed in detail in Section 4.1.3, are presented as percentages of the total soil composition while the spectral gamma data are presented in picoCuries per gram (pCi/g).]* This correlation is particularly evident in the Plio-Pleistocene unit from 180 to 205 ft.

The spectral gamma and XRF data for uranium do not correlate as well as for potassium. Two distinct features found in the plot of the uranium concentrations from the XRF data are not reflected in the spectral gamma data. These are the marked increase in the uranium concentration observed at approximately 170 ft and the general decrease in the uranium concentration observed for the Plio-Pleistocene unit. A possible explanation for these discrepancies between the data is that while the small amount of uranium in the soils is detectable with the spectral gamma log, the still smaller changes in the uranium concentrations may not be detectable with the spectral gamma log.

The thorium data from the spectral gamma tend to correlate with the thorium XRF data better than the uranium data. The change in thorium concentrations observed from the XRF data in for the Plio-Pleistocene unit is also observed in the spectral gamma data for thorium in this same interval.

4.1.2.2 Hanford Unit Geophysical Log Responses

The Hanford Unit is described on the lithologic log from ground surface to 181 ft-bgs. It includes both the Hanford Unit 1 (ground surface to 67 ft-bgs) and Hanford Unit 2 (67 to 181 ft-bgs). Within this interval, two distinct zones are observed in the geophysical log data marked primarily by a change in the soil moisture.

From 50 to 143 ft-bgs the soil moisture indicated by the neutron soil-moisture log shown on Plate 3 is typically 4% by volume. However, discrete zones ranging in thickness from 2 to 4 ft are observed approximately every 10 ft with soil moisture increasing to as much as 8% by volume. The total gamma count for this interval shown on Plate 1 is relatively uniform, ranging from 250 to 300 counts per second (cps). Slight increases in the total gamma count are observed which correlate with the zones of increased soil moisture. The total gamma count for this interval appears to be dominated by the potassium-40 in the sediments, which typically is around 15 pCi/g. The uranium activity is around 2 pCi/g and the thorium activity is around 1 pCi/g.

The interval from 143 to 181 ft-bgs is characterized by a noticeable increase in the soil moisture. The average soil moisture reported from the neutron log in this interval is approximately 8% by volume as compared the 4% by volume for the interval above (50 to 143 ft-bgs). The discrete zones of increased soil moisture observed in the upper interval are also present within this interval, however, these zones have significantly higher soil moisture, some as much as 14% by volume as reported by the neutron log, and occur more frequently (approximately every 5 ft) and range in thickness from 4 to 5 ft.

In the interval from 143 to 181 ft-bgs, the total gamma count has more variability than the interval above (50 to 143 ft-bgs) with low values typically around 250 cps and several zones showing total gamma counts up to 350 cps. The total gamma count in this interval (143 to 181 ft-bgs) appears to vary due to changes in the uranium and thorium activity more than in the interval above (50 to 143 ft-bgs). For example, the interval from 166 to 181 ft-bgs is associated with an increase in thorium activity, while a decrease in the total gamma count observed from 155 to 158 ft-bgs appears to be related to an observed decrease in the uranium and thorium activities.

4.1.2.3 Plio-Pleistocene Geophysical Log Responses

The Plio-Pleistocene unit is composed of two subunits; the Palouse soils (181 to 186 ft-bgs), and a caliche layer (186 to 205 ft-bgs). These two subunits have distinct geophysical signatures. The Palouse soils are characterized by an increased total gamma count from approximately 300 cps to 350 cps. This increase is related to the uranium and thorium activity. Additionally, the Palouse soils exhibit a decrease in potassium-40 activity. The neutron soil-moisture data indicates the soil moisture above the Palouse soils is approximately 14% by volume and then it decreases rapidly in the Palouse soils to 4% by volume at the base of the unit.

The caliche layer is characterized by a significant decrease in the total gamma count to around 200 cps from the overlying Palouse soils. This change is related to a decrease in the potassium-40 and thorium activities. The soil moisture increases at the top of the caliche to about 12% by volume compared to the 4% soil moisture by volume observed in the overlying Palouse soils. The soil moisture decreases in the caliche layer to 4% at the base of the unit.

4.1.2.4 Upper Ringold Geophysical Log Responses

The Upper Ringold formation from 205 to 220 ft-bgs, directly below the caliche layer of the Plio-Pleistocene, is characterized by a significant increase in soil moisture to approximately 15% by volume.

This interval also exhibits an increase in the total gamma count (350 cps) over the total gamma count observed for the caliche layer. This increase is associated with an increase of the potassium-40 and thorium. The uranium activity for these soils appears to be steadily decreasing from 2 pCi/g to 1 pCi/g. Two zones of increased soil moisture characterize the remaining portion of the Upper Ringold formation that was logged: the first at 225 ft-bgs and the second at 235 ft-bgs. The remaining sediments have soil moisture levels less than 4% by volume. The total gamma count observed for these sediments increases slightly at 235 ft-bgs, possibly associated with thorium.

4.1.3 Laboratory Analyses of Soil Samples

Split-spoon samples and grab samples obtained during the drilling of well 299-W19-43 were submitted to Battelle Labs in Richland, Washington for analysis of the sediment, one-to-one sediment to water extracts (Rhoades, J.D., 1996), and groundwater according to the methods outlined in Table 3-1 and Table 3-1. The results of these analyses are presented and discussed in the following sections.

4.1.3.1 Physical Properties and Soil Chemistry

The physical properties of the soils measured in the laboratory included bulk density; particle density; surface area; and particle size (sieve analysis). The results of the physical property analyses are presented in Table 4-1 and shown on Plate 1.

Table 4-1. Laboratory analytical results for soil chemistry and physical properties.

Sample Description	Approximate Depth (ft)	Bulk Density (g/cm ³)	Average Particle Density (g/cm ³)	BET Surface Area (m ² /g)	EGM Surface Area (m ² /g)
MSE-CORE-101B	21.5	1.67	3.17	12.70	
MSE-CORE-102B	51.4	2.02	2.64	3.39	
MSE-CORE-103B	81.6	2.00	2.62	3.32	20.16
MSE-CORE-104B	111.3	1.89	2.44	4.44	
MSE-CORE-105B	141.5	1.83	2.55	3.89	
MSE-CORE-106B	171.5	1.64	2.60	15.25	
MSE-CORE-107A	182.4	1.78	2.19	6.40	
MSE-CORE-108A	185.1	1.85	2.76	6.76	
MSE-CORE-108B	186.1	2.00	3.46	12.36	
MSE-CORE-109A	187.6	1.98	2.55	11.39	
MSE-CORE-109B	188.8	1.94	2.40	17.87	
MSE-CORE-110A	189.5	1.88	2.74	16.71	
MSE-CORE-110B	190.6	1.89			
MSE-CORE-111 RS	192.1		2.50	22.99	
MSE-CORE-111A	192.6	1.88	2.72	23.55	58.85
MSE-CORE-111B	193.6	1.94	2.84	19.69	
MSE-CORE-112B	195.8	1.94	2.57	16.03	
MSE-CORE-113B	198.3	1.93	2.81	15.74	
MSE-CORE-115A	202.6	1.95	2.87	16.71	
MSE-CORE-116B	206	1.97	2.57	17.09	
MSE-CORE-117B	208.6	1.78	2.49	12.13	
MSE-CORE-118B	209.8	1.77		12.39	
MSE-CORE-118 RS	210.4		2.49		
MSE-CORE-119B	231.4	1.39	2.51	4.06	
MSE-CORE-120B	246.5	1.73	2.56	3.57	11.92
MSE-CORE-122A	261.5	2.41	2.74	3.56	
MSE-CORE-123A	271.5	2.20	2.58	3.03	3.18

The soil chemistry analyses included bulk mineralogy measured using x-ray diffraction (XRD), the elemental composition of the soil determined from x-ray-fluorescence (XRF), the carbon content of the soil (this includes total carbon, inorganic carbon, and organic carbon). The results of the soil chemistry analyses are presented in Table 4-2, Table 4-3, Table 4-4 respectively. The results of the XRD and carbon analyses are also shown graphically on Plate 1. The XRF data are shown graphically on Plate 2.

Table 4-2. Laboratory analytical results for soil particle size measurements.

Sample Description	Depth (ft)	Percent Passing Sieve #:							Soil Composition (wt %)			
		10	18	35	60	140	200	270	Gravel	Sand	Silt	Clay
MSE-CORE-101B	21.5	99.4	93.7	46.5	19.5	12.9	11.5	10.1	0.6	89.3	4.8	5.3
MSE-CORE-102B	51.4	100.0	98.4	80.8	48.3	21.0	17.0	14.8	0.0	85.2	6.0	3.4
MSE-CORE-103B	81.6	99.2	94.7	68.3	31.6	18.7	16.2	13.9	0.8	85.3	7.1	1.7
MSE-CORE-104B	111.3	99.8	98.5	96.1	93.9	63.0	44.6	31.4	0.2	68.5	17.5	3.7
MSE-CORE-105B	141.5	100.0	100.0	99.9	97.0	49.5	31.6	22.8	0.0	77.2	8.2	4.1
MSE-CORE-106B	171.5	100.0	100.0	99.9	99.9	99.7	99.2	93.8	0.0	6.2	73.9	8.6
MSE-CORE-107A	182.4	100.0	100.0	99.9	99.8	98.7	95.5	86.4	0.0	13.6	57.7	4.1
MSE-CORE-108A	185.1	95.8	94.7	89.3	77.6	55.6	45.5	32.7	4.2	63.1	28.0	5.3
MSE-CORE-108B	186.1	94.3	91.8	87.2	76.8	55.8	44.4	35.7	5.7	58.6	18.8	8.3
MSE-CORE-109A	187.6	93.4	91.0	87.8	77.7	60.6	50.8	39.8	6.6	53.6	28.2	8.5
MSE-CORE-109B	188.8	55.4	55.4	48.8	43.5	36.6	32.4	29.0	44.6	26.4	10.4	2.6
MSE-CORE-110A	189.5	78.1	68.0	58.6	44.2	25.6	18.8	14.5	21.9	63.6	6.0	6.8
MSE-CORE-111 RS	192.1	93.1	86.5	74.8	58.0	32.7	21.0	13.0	6.9	80.1	8.3	3.4
MSE-CORE-111A	192.6	87.0	79.5	70.3	57.0	36.5	29.8	23.8	13.0	63.2	10.4	11.1
MSE-CORE-111B	193.6	81.8	69.8	60.0	48.8	29.4	23.4	20.3	18.2	61.6	8.4	7.8
MSE-CORE-112B	195.8	88.6	83.0	76.1	64.4	47.5	42.5	38.2	11.4	50.4	23.5	13.3
MSE-CORE-113B	198.3	95.7	91.4	83.4	66.9	53.9	42.2	41.6	4.3	54.1	11.0	7.9
MSE-CORE-115A	202.6	93.1	89.7	81.5	68.0	48.7	40.2	33.9	6.9	59.3	11.4	13.6
MSE-CORE-116B	206.0	99.8	99.7	99.3	98.8	98.2	98.0	97.3	0.2	2.6	87.4	4.2
MSE-CORE-117B	208.6	100.0	100.0	100.0	99.9	99.5	99.4	98.4	0.0	1.6	89.6	7.6
MSE-CORE-118 RS	210.4	95.7	95.5	95.5	95.5	95.0	91.4	78.6	4.3	17.1	61.7	9.0
MSE-CORE-119B	231.4	100.0	100.0	100.0	99.9	83.2	53.2	28.3	0.0	71.6	24.5	1.7
MSE-CORE-120B	246.5	97.0	96.6	94.0	86.4	41.6	29.0	23.8	3.0	73.1	17.0	5.5
MSE-CORE-122A	261.5	100.0	58.7	33.3	18.3	7.8	6.1	5.0	0.0	95.0	6.4	2.9
MSE-CORE-123A	271.5	100.0	79.6	70.4	51.3	17.1	14.4	13.2	0.0	86.8	2.4	2.1

4.1.3.1.1 Bulk Density and Particle Density

The bulk density and particle density presented in Table 4-1 and shown on Plate 1 were measured from core sub-samples taken during drilling. The average bulk density for the soils is 1.85 g/cc, a slight increase in the bulk density is observed for the Plio-Pleistocene unit. The average particle density, also shown on Plate 1, is 2.65 g/cc, which is the density of quartz. The XRD data (which are discussed below) indicate that quartz is the dominant mineral found in the soils, which agrees with the particle density data. From the bulk density and particle density, the average formation porosity can be calculated using Equation 4-1 below.

$$\theta = 1 - \frac{\rho_B}{\rho_P} \quad (4-1)$$

Where θ is the porosity of the formation, ρ_B is the bulk density of the soil, and ρ_P is the particle density of the soil.

Table 4-3. Bulk Chemical Analysis of Soils from XRF.

Sample Description	Depth (ft)	Weight %																		
		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	SrO	BaO	NiO	CuO	ZnO	ZrO ₂	UO ₃
MSE-CORE-101B	21.5	2.723	3.647	13.453	60.544	0.683	0.370	0.048	1.491	6.394	1.783	0.137	9.846	0.042	0.089	0.003	0.002	0.007	0.021	0.001
MSE-CORE-102B	51.4	2.790	1.790	13.349	68.459	0.605	0.375	0.045	2.340	3.097	0.446	0.052	3.188	0.040	0.093	0.002	0.002	0.004	0.021	0.001
MSE-CORE-103B	81.6	2.561	2.752	13.425	70.278	0.619	0.418	0.046	2.457	3.018	0.502	0.056	3.393	0.042	0.105	0.002	0.002	0.001	0.018	0.001
MSE-CORE-104B	111.3	1.968	3.631	13.283	67.026	0.595	0.392	0.045	2.381	3.293	0.584	0.064	4.100	0.038	0.086	0.003	0.002	0.006	0.032	0.002
MSE-CORE-105B	141.5	2.359	3.813	14.347	67.839	0.631	0.409	0.047	2.405	3.512	0.621	0.077	4.357	0.045	0.107	0.003	0.003	0.006	0.034	0.001
MSE-CORE-106B	171.5	1.294	4.808	16.205	62.647	0.621	0.400	0.047	2.738	3.624	0.734	0.075	5.383	0.027	0.090	0.004	0.004	0.008	0.035	0.003
MSE-CORE-107A	182.4	1.914	3.946	13.535	65.856	0.618	0.424	0.048	2.321	2.751	0.684	0.066	4.264	0.038	0.099	0.004	0.003	0.006	0.048	0.002
MSE-CORE-108A	185.1	2.116	3.797	13.359	61.292	0.563	0.323	0.042	1.811	6.693	1.138	0.085	5.769	0.046	0.067	0.004	0.003	0.007	0.049	0.001
MSE-CORE-108B	186.1	1.294	2.735	9.548	37.703	0.801	0.414	0.046	1.233	22.308	1.283	0.169	5.576	0.039	0.058	0.003	0.003	0.006	0.030	0.001
MSE-CORE-109A	187.6	1.766	3.830	10.776	54.696	0.676	0.400	0.047	1.647	11.954	1.143	0.102	5.858	0.040	0.063	0.004	0.003	0.006	0.036	0.001
MSE-CORE-109B	188.8	0.687	3.697	4.768	24.488	0.895	0.422	0.044	0.756	40.530	0.645	0.119	3.371	0.038	0.039	0.002	0.002	0.003	0.015	0.001
MSE-CORE-110A	189.5	1.685	4.012	10.751	45.319	0.898	0.370	0.047	1.056	16.818	1.748	0.133	7.753	0.043	0.072	0.003	0.002	0.008	0.023	0.001
MSE-CORE-111 RS	190.6	1.914	4.327	10.550	47.494	0.824	0.400	0.046	1.072	17.998	1.401	0.119	7.116	0.041	0.063	0.002	0.003	0.007	0.023	0.001
MSE-CORE-111A	192.1	1.968	4.095	13.434	53.484	1.037	0.390	0.049	1.319	9.692	2.237	0.154	10.651	0.038	0.074	0.004	0.003	0.010	0.030	0.001
MSE-CORE-111B	192.6	2.265	4.858	13.516	56.094	0.722	0.395	0.049	1.329	10.083	1.796	0.130	8.367	0.041	0.068	0.003	0.003	0.008	0.025	0.001
MSE-CORE-112B	195.8	0.795	2.918	7.016	31.320	1.219	0.355	0.043	0.915	30.969	0.924	0.079	5.018	0.036	0.047	0.003	0.003	0.005	0.021	0.001
MSE-CORE-113B	198.3	1.995	3.780	10.984	51.915	0.818	0.397	0.048	1.254	14.454	1.404	0.103	6.841	0.042	0.067	0.002	0.002	0.007	0.023	0.001
MSE-CORE-115A	202.6	1.483	3.797	10.361	46.139	1.007	0.378	0.047	1.136	19.169	1.238	0.094	6.473	0.040	0.058	0.003	0.003	0.006	0.024	0.001
MSE-CORE-116B	206.0	2.197	5.239	13.075	59.267	0.637	0.376	0.045	2.406	6.273	0.732	0.087	5.219	0.072	0.150	0.005	0.003	0.007	0.033	0.001
MSE-CORE-117B	208.6	2.467	4.443	15.588	62.754	0.661	0.409	0.048	2.923	3.190	0.842	0.113	5.501	0.073	0.161	0.006	0.004	0.007	0.031	0.001
MSE-CORE-118 RS	209.8	2.372	4.841	14.669	63.182	0.637	0.410	0.048	2.779	4.417	0.737	0.100	5.336	0.055	0.127	0.005	0.004	0.006	0.030	0.003
MSE-CORE-119B	231.4	2.238	2.470	12.437	74.949	0.610	0.365	0.044	1.954	2.001	0.503	0.049	3.306	0.039	0.075	0.002	0.002	0.004	0.033	0.001
MSE-CORE-120B	246.5	2.831	1.757	12.061	80.254	0.608	0.375	0.046	2.057	1.716	0.404	0.046	2.793	0.045	0.089	0.002	0.001	0.001	0.022	0.001
MSE-CORE-122A	261.5	3.491	2.653	14.121	73.380	0.660	0.419	0.048	1.812	3.974	0.574	0.073	4.321	0.041	0.076	0.002	0.004	0.006	0.018	0.001
MSE-CORE-123A	271.5	3.370	2.205	13.579	73.808	0.628	0.408	0.047	2.106	2.948	0.573	0.064	4.057	0.049	0.095	0.003	0.002	0.005	0.027	0.001

The average formation porosity calculated using Equation 4-1 is 30%. This is a typical value for sandy soils and well within the expected range of 25% to 50% given for sandy soils (Freeze and Cherry, 1979).

The particle surface area of the soils was measured using Brunauer, Emmett, and Teller (BET) (Carter et al, 1986) analysis for the core samples; these data are presented in Table 4-1 and graphically on Plate 1. The average surface area measured for the samples is 11.40 m²/g. Also included in Table 4-1 are surface area measurements obtained using the ethylene glycol monoethyl ether (EGM) method (Carter et al, 1986). Originally, this method was to be applied to radioactive samples. When the samples were determined to be non-radioactive, these measurements were made as a reference in case future work required this type of measurement process.

4.1.3.1.2 Particle Size Analysis

A sieve analysis was conducted on the core samples. The results are listed in Table 4-2. Also listed are the percentages of gravel, sand, silt, and clay as determined by the laboratory for each of the soil types. The results of the analyses indicate that the soils are generally composed of a sand sized fraction, typically comprising 50% to 95% of the sample. At 188 ft the soil is dominated by a gravel fraction and at two intervals, (171–182, and 206 to 210 ft) the soils are primarily silt.

It should be noted that although the results from the laboratory do not always total to 100% for the soil composition, the results are close enough to reasonably determine the soil type. As the results indicate, one size fraction is typically dominant in each soil sample.

The results of the sieve analysis were used to estimate saturated hydraulic conductivities for the soils. Both the Hazen method (Fetter, 1988) and the Krumbein and Monk method (Krumbein and Monk, 1943) were used for these estimates. The results are plotted on Plate 1 along with the geometric mean of the results from the two estimations. The estimated saturated hydraulic conductivity is generally between 1×10^{-2} cm/sec and 1×10^{-3} cm/sec for the Hanford units, it decreases to 1×10^{-3} cm/sec and lower in the Plio-Pleistocene unit and then increases to 1×10^{-2} cm/sec again in the Ringold unit. The discrepancy between the results obtained from the two methods may be due to the inherent assumptions contained in the individual methods.

4.1.3.1.3 Elemental Composition of Soil from X-Ray-Florescence (XRF)

The results from the XRF analysis of the soil composition are presented in Table 4-3 and shown graphically on Plate 2. The soil composition is relatively uniform in the Hanford units. The data indicate that silicon; most probably in the form of a silicate mineral, composes the bulk of the sediment. Iron is also found in the soils in abundance, ranging from 3% to 10% by weight. There is a slight increase in the iron content in the Plio-Pleistocene unit. Aluminum is also abundant in the soils, typically comprising approximately 10% to 12 % by weight. In the Plio-Pleistocene unit, aluminum decreases slightly. The composition of the Ringold unit appears to be similar to the Hanford units with some minor variation.

4.1.3.1.4 Bulk Mineralogy from X-Ray Diffraction (XRD)

The bulk mineralogy of the soils was determined using x-ray diffraction (XRD). The results are presented in Table 4-4 as the relative intensities of the major reflections to the Quartz 3.34 Angstrom (Å) reflection. These results are also shown graphically on Plate 1. This is a relative indicator of mineral abundance. The XRD data indicate that quartz is the dominant mineral assemblage in the soils, making

up approximately 60% or more of the soil. Feldspars (primarily plagioclase and potassium feldspar) make up most of the remaining portion of the soils. Other minerals present in the soils in lesser amounts include calcite, amphibole, chlorite, mica, and other phyllosilicates.

Table 4-4. Bulk Mineralogical Results from XRD Analysis of Soils.

Sample Description	Depth (ft)	Relative Intensities of Major Reflections of Minerals to the Quartz 3.34 Å Reflection (Qualitative Indicator of Mineral Abundances)							
		Quartz	Plagioclase	K-Spar	Calcite	Amphibole	Chlorite	Mica	Clay (Represents Phyllosilicates)
MSE-CORE-101B	21.5	1	0.86	0.14	0.00	0.01	0.01	0.05	0.02
MSE-CORE-102B	51.4	1	0.39	0.19	0.02	0.02	0.01	0.06	0.01
MSE-CORE-103B	81.6	1	0.29	0.15	0.01	0.02	0.01	0.05	0.01
MSE-CORE-104B	111.3	1	0.20	0.08	0.05	0.11	0.00	0.05	0.01
MSE-CORE-105B	141.5	1	0.32	0.12	0.01	0.07	0.01	0.05	0.01
MSE-CORE-106A	170.6	1	0.13	0.04	0.02	0.02	0.02	0.12	0.02
MSE-CORE-107A	182.4	1	0.16	0.05	0.00	0.06	0.01	0.07	0.01
MSE-CORE-108A	185.1	1	0.40	0.05	0.04	0.16	0.02	0.07	0.01
MSE-CORE-108B	186.1	1	0.42	0.06	0.34	0.14	0.02	0.08	0.01
MSE-CORE-109B	188.8	1	2.44	0.34	2.73	0.08	0.09	0.24	0.03
MSE-CORE-110A	189.5	1	0.68	0.43	0.39	0.05	0.02	0.05	0.01
MSE-CORE-111A	192.6	1	0.57	0.09	0.39	0.06	0.01	0.03	0.01
MSE-CORE-111B	193.6	1	1.77	0.33	0.00	0.15	0.00	0.03	0.03
MSE-CORE-112B	195.8	1	1.16	0.18	1.16	0.14	0.01	0.09	0.02
MSE-CORE-113B	198.3	1	0.86	0.12	0.20	0.11	0.02	0.05	0.01
MSE-CORE-115B	203.6	1	0.60	0.08	0.38	0.08	0.02	0.05	0.04
MSE-CORE-116B	206.0	1	0.32	0.12	0.02	0.07	0.07	0.05	0.01
MSE-CORE-117B	208.6	1	0.36	0.14	0.02	0.07	0.04	0.03	0.01
MSE-CORE-118B	209.8	1	0.53	0.08	0.08	0.07	0.04	0.09	0.01
MSE-CORE-119B	231.4	1	0.16	0.07	0.00	0.02	0.01	0.03	0.01
MSE-CORE-120B	246.5	1	0.14	0.06	0.00	0.02	0.01	0.04	0.01
MSE-CORE-122A	261.5	1	0.24	0.06	0.00	0.03	0.00	0.01	0.00
MSE-CORE-123A	271.5	1	0.28	0.18	0.00	0.01	0.00	0.03	0.01

The composition of the clay fraction (note: this is the clay sized particles and not the clay minerals) taken from the XRD data is presented in Table 4-5. The clay-sized fraction of the soil is primarily composed of smectite, chlorite, mica, and quartz.

4.1.3.1.5 Soil Carbon Content

The total carbon content of the soil was analyzed in addition to determining the organic and inorganic carbon content of the soil. The results are presented in Table 4-6. The results of the carbon analyses are also presented graphically on Plate 1.

The primary form of carbon in the soils is inorganic carbon. The total soil carbon content ranges from 0.03% to 6.57% with the median value equal to 0.34%. The organic carbon content of the soils ranged from none to 0.45%. The median organic carbon content is 0.05%. The inorganic carbon, which makes up most of the carbon in the soils, ranges from none to 6.11%. The median value for the inorganic carbon is 0.30%.

Table 4-5. Bulk mineralogical results from XRD analysis of clay fraction in soils.

Sample Description	Approximate Depth	Relative Intensities of Major Reflections of Minerals to the Quartz 3.34 Å Reflection (Qualitative Indicator of Mineral Abundances)							
		Smectite	Chlorite	Mica	Kaolinite	Quartz	Feldspar	Amphibole	Calcite
MSE-CORE-101B	21.5	na	na	na	na	na	na	na	na
MSE-CORE-102B	51.4	0.81	0.77	1	Y	Y	tr	Y	
MSE-CORE-103B	81.6	0.4	0.64	1.00	Y	Y	tr	Y	
MSE-CORE-104B	111.3	0.49	0.67	1	Y	Y	tr	Y	
MSE-CORE-105B	141.5	0.74	1.01	1.00	Y?	Y	Y		
MSE-CORE-106A	170.6	0.82	0.58	1	Y	Y	Y		tr
MSE-CORE-107A	182.4	0.67	0.59	1.00	Y	Y	tr	Y	
MSE-CORE-108A	185.1	tr?	0.46	1	Y	Y	Y	Y	Y
MSE-CORE-108B	186.1	tr?	Y	Y		tr?	tr	?	Y1
MSE-CORE-109B	188.8		Y	Y		Y	Y		Y1
MSE-CORE-110A	189.5		Y	Y	Y	Y	Y		Y1
MSE-CORE-111A	192.6	tr	Y	Y	Y?	Y	Y	Y	Y1
MSE-CORE-111B	193.6	tr	Y	Y		Y	Y	tr	Y1
MSE-CORE-112B	195.8	tr	1.44	1		Y	Y		Y
MSE-CORE-113B	198.3		Y	Y		Y	Y		Y1
MSE-CORE-115B	203.6	tr?	Y	Y		tr	tr		Y1
MSE-CORE-116B	206.0	4.18	2.6	1	Y	Y	Y	Y	
MSE-CORE-117B	208.6	2.8	1.76	1	Y	Y	Y	Y	
MSE-CORE-118B	209.8	1.92	0.96	1.00	Y	Y	Y	Y	
MSE-CORE-119B	231.4	1.12	0.64	1.00	Y	Y	Y	Y	
MSE-CORE-120B	246.5	0.44	2.19	1	Y?	Y	Y	Y	
MSE-CORE-122A	261.5	tr	3.35	1.00		Y	Y	Y	Y
MSE-CORE-123A	271.5	tr	4.65	1	?	Y	Y	Y	

Y – Mineral present in minor amounts

tr – Mineral present in trace amounts

? – Uncertainty in measurement

na – Not analyzed

4.1.3.2 Soil Moisture and Sediment-Water Extract Chemistry

Soil moisture and one-to-one sediment to water extracts obtained from selected soil cores were analyzed for: pH; Eh; conductivity; alkalinity; cations and anions, uranium, and carbon concentrations. Results for these analyses are presented in this section in addition to a discussion of the soil moisture in the soils.

Soil Moisture

The soil moisture data, shown on Plate 3, were obtained from two different sample types and from the neutron moisture log. The first soil moisture data presented in Table 4-7 and identified as “can” samples are from grab samples taken during drilling and placed immediately into tin cans that were sealed. These samples were specifically acquired for a soil moisture determination. The second set of soil moisture data shown in Table 4-7 is from sub-samples taken from the core samples. These two data sets were combined and plotted on Plate 3 along side the neutron soil-moisture data and soil moisture data obtained from the CPT electrical conductivity data.

Table 4-6. Laboratory analytical results for soil carbon content.

Sample Description	Approximate Depth (ft)	Total Carbon (wt %)	Organic Carbon (wt%)	Inorganic Carbon (wt%)
MSE-CAN-001	5	0.66	0.21	0.45
MSE-CAN-002	10	0.35	0.05	0.30
MSE-CAN-003	15	0.07	0.02	0.05
MSE-CAN-004	20	0.24	0.05	0.19
MSE-CAN-005	25	0.11	0.03	0.08
MSE-CAN-023	215	0.03	0.01	0.02
MSE-CORE-101B	21.5	0.13	0.04	0.09
MSE-CORE-102B	51.4	0.34	0.04	0.30
MSE-CORE-103B	81.6	0.25	0.02	0.23
MSE-CORE-104B	111.3	0.29	0.04	0.25
MSE-CORE-105B	141.5	0.25	0.03	0.22
MSE-CORE-106B	171.5	0.54	0.07	0.47
MSE-CORE-107A	182.4	0.26	0.05	0.21
MSE-CORE-108A	185.1	0.67	0.07	0.60
MSE-CORE-108B	186.1	2.67	0.15	2.52
MSE-CORE-109A	187.6	1.77	0.08	1.69
MSE-CORE-109B	188.8	6.57	0.45	6.11
MSE-CORE-110A	189.5	2.51	0.04	2.49
MSE-CORE-111 RS	192.1	0.44	0.06	0.36
MSE-CORE-111A	192.6	2.15	0.07	2.08
MSE-CORE-111B	193.6	0.67	0.05	0.62
MSE-CORE-112B	195.8	4.59	0.15	4.44
MSE-CORE-113B	198.3	1.56	0.08	1.48
MSE-CORE-115A	202.6	2.70	0.03	2.67
MSE-CORE-116B	206	0.30	0.00	0.30
MSE-CORE-117B	208.6	0.11	0.01	0.10
MSE-CORE-118B	209.8	1.65	0.34	1.31
MSE-CORE-119B	231.4	0.05	0.02	0.03
MSE-CORE-120B	246.5	0.05	0.05	0.00
MSE-CORE-122A	261.5	0.07	0.03	0.04
MSE-CORE-123A	271.5	0.05	0.03	0.02

The volumetric soil moisture was calculated from the weight percent soil moisture measured in the laboratory. It appears that these values differ from the volumetric soil moisture determined using the neutron-soil moisture log by a factor of bulk density. This discrepancy needs to be resolved through reexamination of the procedures used by each vender. This will be completed in FY03. However, the general trends in soil moisture are similar between the data sets.

In the Hanford unit where the measurements overlap (50 to 60 ft bgs), the neutron soil-moisture data and soil-moisture data from the CPT conductivity measurements are offset by approximately 10%, with CPT data being greater.

The data from both the neutron soil-moisture log and the laboratory show a significant increase immediately below the Plio-Pleistocene unit at approximately 205 to 230 ft. This general level of correlation between the data suggests the measurements are representative of the trends in subsurface soil moisture conditions.

Table 4-7. Soil moisture data.

Sample Description	Approximate Depth (ft)	Soil Moisture (Wt%)	Bulk Density (g/cm3)	Calculated Soil Moisture (vol%)	Neutron Soil Moisture (vol%)
MSE-CAN-001	5.0	4.27	1.9	8.1	N/A
MSE-CAN-002	10.0	3.47	1.9	6.6	N/A
MSE-CAN-003	15.0	2.92	1.9	5.5	N/A
MSE-CAN-004	20.0	5.21	1.9	9.9	N/A
MSE-CAN-005	25.0	3.13	1.9	5.9	N/A
MSE-CAN-006	30.0	4.51	1.9	8.6	N/A
MSE-CAN-007	40.0	2.8	1.9	5.3	N/A
MSE-CAN-008	50.0	2.49	1.9	4.7	0.72
MSE-CAN-009	60.0	2.78	1.9	5.3	3.01
MSE-CAN-010	70.0	2.57	1.9	4.9	2.62
MSE-CAN-011	80.0	2.48	1.9	4.7	2.86
MSE-CAN-012	90.0	3.64	1.9	6.9	3.72
MSE-CAN-013	100.0	2.89	1.9	5.5	2.49
MSE-CAN-014	110.0	5.06	1.9	9.6	3.79
MSE-CAN-015	120.0	3.54	1.9	6.7	5.52
MSE-CAN-016	130.0	4.69	1.9	8.9	4.13
MSE-CAN-017	140.0	3.93	1.9	7.5	4.12
MSE-CAN-018	150.0	7.22	1.9	13.7	4.84
MSE-CAN-019	160.0	22.31	1.9	42.4	14.95
MSE-CAN-020	170.0	9.92	1.9	18.8	6.39
MSE-CAN-021	180.0	15.5	1.9	29.5	12.51
MSE-CAN-022	206.5	17.45	1.9	33.2	13.9
MSE-CAN-023	215.0	18.94	1.9	36.0	15.93
MSE-CAN-024	220.0	12.29	1.9	23.4	4.54
MSE-CAN-025	241.0	5.1	1.9	9.7	2.63
MSE-CAN-026	250.0	8.6	1.9	16.3	6.57
MSE-CAN-027	260.0	5.34	1.9	10.1	17.53
MSE-CORE-101A	20.5	3.83	1.72	6.6	N/A
MSE-CORE-101B	21.5	3.46	1.67	5.8	N/A
MSE-CORE-102A	50.5	3.19	1.85	5.9	1.71
MSE-CORE-102B	51.4	2.77	2.02	5.6	2.53
MSE-CORE-103A	80.6	1.96	1.88	3.7	2.55
MSE-CORE-103B	81.6	2.02	2	4.0	2.59
MSE-CORE-104A	110.6	3.68	1.83	6.7	3.77
MSE-CORE-104B	111.3	7.32	1.89	13.8	4.21
MSE-CORE-105A	140.5	7.68	1.63	12.5	3.38
MSE-CORE-105B	141.5	4.65	1.83	8.5	3.92
MSE-CORE-106A	170.6	5.17	1.65	8.5	5.04
MSE-CORE-106B	171.5	19.54	1.64	32.0	10.2
MSE-CORE-107A	182.4	12.01	1.78	21.4	9.62
MSE-CORE-107B	183.4	11.51	1.5	17.3	6.3
MSE-CORE-108A	185.1	6.71	1.85	12.4	3.96
MSE-CORE-108B	186.1	12.75	2	25.5	6.47
MSE-CORE-109A	187.6	9.84	1.98	19.5	10.59
MSE-CORE-109B	188.8	9.03	1.94	17.5	11.29
MSE-CORE-110A	189.5	6.33	1.88	11.9	11.13
MSE-CORE-110B	190.6	10	1.89	18.9	5.7
MSE-CORE-111 RS	192.1	7.49	1.89	14.2	9.01
MSE-CORE-111A	192.6	9.64	1.88	18.1	9.04
MSE-CORE-111B	193.6	5.79	1.94	11.2	8.92
MSE-CORE-112A	194.8	9.02	1.84	16.6	8.21

Table 4-7. Soil moisture data.

Sample Description	Approximate Depth (ft)	Soil Moisture (Wt%)	Bulk Density (g/cm ³)	Calculated Soil Moisture (vol%)	Neutron Soil Moisture (vol%)
MSE-CORE-112B	195.8	11.12	1.94	21.6	7.66
MSE-CORE-113A	197.3	7.77	1.85	14.4	7.04
MSE-CORE-113B	198.3	6.39	1.93	12.3	5.2
MSE-CORE-114A	200.6	6.43	1.82	11.7	5.32
MSE-CORE-114B	201.5	7.44	1.89	14.1	5.54
MSE-CORE-115A	202.6	8.8	1.95	17.2	5.82
MSE-CORE-115B	203.6	6.24	1.84	11.5	5.28
MSE-CORE-116A	205.4	14.62	1.92	28.1	15.25
MSE-CORE-116B	206.0	18.83	1.97	37.1	14.15
MSE-CORE-117A	207.7	20.33	1.87	38.0	13.56
MSE-CORE-117B	208.6	18.95	1.78	33.7	14.19
MSE-CORE-118A	209.3	17.8	1.68	29.9	15.12
MSE-CORE-118B	209.8	12.43	1.77	22.0	16.03
MSE-CORE-118 RS	210.4	0		0.0	14.16
MSE-CORE-119A	230.3	7.73	1.36	10.5	3.52
MSE-CORE-119B	231.4	4.69	1.39	6.5	10.29
MSE-CORE-120A	245.6	5.36	1.99	10.7	2.45
MSE-CORE-120B	246.5	4.88	1.73	8.4	2.76
MSE-CORE-122A	261.5	10.03	2.41	24.2	17.53
MSE-CORE-122B	260.5	14.37	2.19	31.5	17.53
MSE-CORE-123A	271.5	12.58	2.2	27.7	17.53
MSE-CORE-123B	270.5	12.77	1.85	23.6	17.53

4.1.3.2.2 Sediment-Water Extract pH, Eh, Conductivity, and Alkalinity

The results of the sediment-water extract pH, Eh, conductivity, and alkalinity measurements are presented in Table 4-8 and shown graphically on Plate 3. The pH shown was measured in the laboratory under atmospheric conditions and ranges from 6.7 to 8.1: the average pH value measured in the laboratory was 7.7. The pH values measured in the laboratory will be discussed in Section 4.1.6 as they compare to the pH values determined from the carbon dioxide measurements. The alkalinity was determined from the total inorganic carbon in the soil moisture. The assumption was made that for the pH range; the inorganic carbon would be in the form of bicarbonate (HCO_3). The equivalents of inorganic carbon were determined for each sample and expressed as the carbonate alkalinity value in terms of milli-equivalents per liter. This approach was taken because the alkalinity values determined from the titration data were not repeatable.

4.1.3.2.3 Carbon Concentrations of Sediment-Water Extract

The total carbon concentrations and organic carbon concentrations were measured for the sediment-water extract. The inorganic carbon concentration was calculated by subtracting the organic carbon concentration from the total carbon concentration. The results of the carbon analysis are also included in Table 4-8.

Table 4-8. Laboratory results of sediment-water extract chemistry and physical properties.

Sample Description	Depth (ft)	pH	Eh (mV)	Conductivity (uS/cm)	Carbonate Alkalinity (meq/L)	Total Carbon (%)	Organic Carbon (%)	Inorganic Carbon (%)	Uranium Concentration (ug/L)
MSE-CORE-101B	21.5	7.4	334.9	212		16.97	3.74	13.24	59.68
MSE-CORE-102B	51.4	7.8	354.0	193	1.17	17.36	3.32	14.04	<32.13
MSE-CORE-103B	81.6	7.5	418.9	148	0.90	14.35	3.53	10.82	<51.31
MSE-CORE-104B	111.3	7.8	369.0	238	1.01	16.39	4.23	12.17	20.59
MSE-CORE-106A	170.6	7.6	408.9	487	1.25	20.91	5.93	14.98	9.63
MSE-CORE-108A	185.1	7.9	346.6	260	1.32	19.37	3.50	15.87	157.20
MSE-CORE-108B	186.1	7.5	384.6	291	1.46	24.23	6.72	17.51	239.78
MSE-CORE-110A	189.5	8.0	351.4	224	1.35	18.68	2.50	16.18	66.86
MSE-CORE-112B	195.8	8.0	380.6	299	1.32	21.00	5.18	15.82	131.58
MSE-CORE-113B	198.3	8.0	373.2	214	1.09	17.43	4.36	13.08	162.04
MSE-CORE-116B	206.0	8.0	384.9	284	1.19	19.35	5.06	14.29	<4.87
MSE-CORE-118B	209.8	8.1	403.3	230	1.21	18.85	4.28	14.57	<7.64
MSE-CORE-119B	231.4	6.7	427.2	70	0.27	10.74	7.48	3.26	<21.50
MSE-CORE-120B	246.5	6.8	460.2	231	0.31	8.21	4.54	3.67	<20.69
MSE-CORE-122A	261.5	7.7	372.4	320	0.65	11.17	3.34	7.83	37.58
MSE-CORE-123A	271.5	8.0	372.8	196	0.88	12.13	1.59	10.54	<7.53

4.1.3.2.4 Cations and Anions of Sediment-Water Extract

In addition, the sediment-water extracts were analyzed for cations (see Table 4-9) and anions (see Table 4-10) concentrations. The cation analysis included calcium (Ca^{+2}), potassium (K^{+}), magnesium (Mg^{+2}), and sodium (Na^{+}). The anion analysis included fluorine (F^{-}), chloride (Cl^{-}), bromide (Br^{-}), nitrate (NO_3^{-}), phosphate (PO_4^{-3}), and sulfate (SO_4^{-2}).

Table 4-9. Laboratory results for cation concentrations in the sediment-water extracts.

Sample Description	Approximate Depth (ft)	Concentration (meq/L)			
		Ca^{+2}	K^{+}	Mg^{+2}	Na^{+}
MSE-CORE-101B	21.5	0.408	0.1	0.169	0.921
MSE-CORE-102B	51.4	0.465	0.105	0.23	0.772
MSE-CORE-103B	81.6	0.395	0.093	0.26	0.57
MSE-CORE-104B	111.3	0.759	0.124	0.419	0.764
MSE-CORE-106B	171.5	1.814	0.133	0.92	1.267
MSE-CORE-108A	185.1	0.925	0.103	0.614	0.663
MSE-CORE-108B	186.1	1.643	0.113	1.176	0.829
MSE-CORE-110A	189.5	0.745	0.082	0.627	0.629
MSE-CORE-112B	195.8	1.018	0.087	0.841	0.662
MSE-CORE-113B	198.3	0.778	0.076	0.599	0.576
MSE-CORE-116B	206.0	1.093	0.073	0.814	0.636
MSE-CORE-118B	209.8	0.861	0.085	0.724	0.51
MSE-CORE-119B	231.4	0.158	0.044	0.132	0.287
MSE-CORE-120B	246.5	0.202	0.055	0.124	0.364
MSE-CORE-122A	261.5	1.218	0.153	0.719	0.567
MSE-CORE-123A	271.5	0.766	0.108	0.444	0.365

Table 4-10. Laboratory results for the anion concentrations in the groundwater.

Sample Description	Approximate Depth	Concentration (meq/L)					
		F ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
MSE-CORE-101B	21.5	0.026	0.023	0	0.302	0.004	0.41
MSE-CORE-102B	51.4	0.019	0.208	0.001	0.159	0.003	0.369
MSE-CORE-103B	81.6	0.02	0.057	0	0.073	0.003	0.25
MSE-CORE-104B	111.3	0.023	0.135	0.001	0.218	0.003	0.731
MSE-CORE-106B	171.5	0.019	0.254	0.002	1.79	0.005	1.129
MSE-CORE-108A	185.1	0.014	0.055	0.001	0.54	0.004	0.502
MSE-CORE-108B	186.1	0.019	0.102	0.002	1.069	0.003	1.333
MSE-CORE-110A	189.5	0.046	0.036	0.001	0.471	0	0.275
MSE-CORE-112B	195.8	0.042	0.058	0.002	0.689	0.001	0.604
MSE-CORE-113B	198.3	0.041	0.028	0.001	0.326	0	0.413
MSE-CORE-116B	206.0	0.032	0.064	0.001	0.731	0.001	0.756
MSE-CORE-118B	209.8	0.034	0.041	0.001	0.515	0.001	0.404
MSE-CORE-119B	231.4	0.017	0.021	0.001	0.229	0.004	0.125
MSE-CORE-120B	246.5	0.015	0.029	0.001	0.31	0.004	0.108
MSE-CORE-122A	261.5	0.028	0.11	0	1.903	0	0.132
MSE-CORE-123A	271.5	0.012	0.115	0	0.64	0.003	0.146

4.1.4 Petrographic Analysis of Soil Samples

A petrographic analysis of the soil samples was completed by MSE to provide information for determining the amount and composition of the grain coatings. The analysis was completed using grain mounts made from selected core samples. The samples used to make the grain mounts are indicated on Plate 4. To complete the petrographic analysis, estimates of the percentage of framework and matrix components were made; this was followed by estimates of the composition of the framework, estimate of the percentage of the framework grains with coatings or other alterations, and finally estimates of the grain coating compositions. The framework grains were classified as quartz, feldspar, and other rock fragments. The framework alterations and coatings were classified as goethite-limonite, hematite, clay, carbonate, or magnetite-ilmenite. Observations were also made as to the crystalline nature of the coating (i.e., crystalline or amorphous). A summary of the results of the petrographic analysis is presented as Plate 4.

4.1.4.1 Hanford Soils

The soils from the Hanford Units are typically unconsolidated rock fragments with some grains of quartz and feldspar. Generally, 25 to 50% of the grains have some type of alteration or coatings. These coatings are dominantly composed of iron in the form of a magnetite or ilmenite with lesser amounts of goethite and limonite. Minor amounts of hematite are also present. There is also some clay and carbonate coatings present, but these generally make up only 25% of the total grain coating. An exception to these observations is near the base of the Hanford Unit 2 directly above the Plio-Pleistocene unit. The entire soil framework is observed to have a coating, which is primarily composed of clay followed by carbonate minerals and hematite. Minor amounts (less than 10% each) of the goethite-limonite and magnetite-ilmenite mineral phases are observed in these sediments.

4.1.4.2 Plio-Pleistocene Unit

The Plio-Pleistocene unit is characterized by a high degree of consolidation; typically, 30% or more of the soil composition was some form of matrix cement. The framework minerals consisted of quartz and feldspar with lesser amounts of other rock fragments. Due to the high degree of cementation, all of the

grains had some form of coating. The coatings were primarily composed of clays and carbonate minerals. Very little iron was observed as a grain coating.

4.1.4.3 Ringold Soils

The Ringold soils are typically unconsolidated materials composed of primarily quartz grains with lesser amounts of feldspars and other rock fragments. There is very little coating or other alteration of the grains (less than 10%), but where it is present; it is almost entirely a form of iron. The grain coatings and alteration in the Upper Ringold is composed of goethite and limonite with minor amounts of hematite, clay, and magnetite/ilmenite. The Ringold Unit E gravels are characterized by coatings of magnetite/ilmenite and with lesser amounts of goethite/limonite.

4.1.5 Citrate-Bicarbonate-Dithionite (CBD) Extract Results

Eight soil samples were analyzed using the citrate-bicarbonate-dithionite (CBD) extraction method to determine the amount of extractable aluminum, iron, and manganese oxide in the soils. A literature review indicated that iron oxides and hydroxides are the primary sorbents of uranium in most soils; therefore, an investigation into the amount and type of iron oxides was initiated. In conjunction with the petrographic analysis of the sediments, a technique was needed to determine the total amount of free iron oxides (both crystalline and amorphous) in the sediments. To accomplish this, the CBD extraction method was selected based on literature reviews related to uranium adsorption studies using surface complexation modeling (Loeppert and Inskeep, 1996; Payne, 1999; and Barnett et al, 2002). By applying the relative percentages of the various iron oxides observed in the petrographic study to the amount of free iron oxide extracted from the sediments using the CBD extraction method, the mass of the different iron oxides could be determined. In addition to the amount of iron in the soil, the amount of aluminum and manganese oxides were also measured. The results of the CBD analysis indicating the relative amounts of Al, Fe, and Mn present in the soils as oxides and hydroxides are presented in Table 4-11.

Table 4-11. Laboratory results from citrate-bicarbonate-dithionite analysis.

Sample Description	Approximate Depth (ft)	Concentration (mg/kg) in Soil		
		Al	Fe	Mn
MSE-CORE-101B	21.5	81 (79)	1660 (1500)	68 (112)
MSE-CORE-104B	111.3	124	2980	85
MSE-CORE-106B	171.5	172	3760	56
MSE-CORE-107A	182.4	221	4230	89
MSE-CORE-112B	195.7	169 (75)	1640 (1290)	59 (52)
MSE-CORE-119B	231.4	146 (102)	3850 (2780)	106 (110)
MSE-CORE-120B	246.5	116	2460	77
MSE-CORE-123B	271.5	56	1300	42

Values in parentheses are from the second lab and shown for comparison purposes.

Two independent laboratories following the procedure outlined in Loeppert and Inskeep (1996) completed the CBD analyses. The results compared well, suggesting the analyses were representative of the total free iron in the soils. The results were also compared to those reported by Barnett et al (2002), however, the results reported by Barnett appeared to be an order of magnitude greater than the results obtained from the two laboratories. This may be due to the fact that the samples analyzed by Barnett were taken from an outcrop. Potentially the outcrop material may have been more weathered than the samples acquired from the borehole, resulting in a greater amount of iron oxide weathering products.

4.1.6 Carbon Dioxide Sampling Results

The results of the soil gas sampling are presented in Table 4-12 as the average CO₂ concentrations measured in the borehole at discrete depth intervals. These results are also shown on Plate 3. As previously discussed, the CO₂ concentration in the soil gas is a critical parameter in determining uranium sorption. The CO₂ concentrations were measured in the field using a CO₂ analyzer and the soil-gas sampling system designed and built by MSE.

Table 4-12. Calculated pH values compared to laboratory pH measurements.

Approximate Depth (ft)	PCO ₂ (ppm)	Alkalinity (meq/L)	pH Calculated	pH Lab Measurement
21.5	4445	1.1	7.1	7.4
51.4	5559	1.17	7.0	7.8
81.6	14299	0.9	6.5	7.5
111.3	17959	1.01	6.5	7.8
170.6	8838	1.25	6.8	7.6
185.1	8405	1.32	6.9	7.9
186.1	8405	1.46	6.9	7.5
189.5	8405	1.35	6.9	8.0
195.8	7971	1.32	6.9	8.0
198.3	7258	1.09	6.9	8.0
206	6544	1.19	7.0	8.0
209.8	9002	1.21	6.8	8.1
231.4	4681	0.27	6.5	6.7
246.5	12699	0.31	6.1	6.8
261.5	12699	0.65	6.4	7.7
271.5	12699	0.88	6.5	8.0

The process used to determine the CO₂ concentration in the soil gas is shown schematically in Figure 4-1. The plot of CO₂ concentration as a function of time is representative of the data obtained at each discrete depth interval. The initial data shown from 0 to approximately 0.20 hours represent measurements made of the CO₂ concentrations of atmospheric air made with the CO₂ meter disconnected from the soil gas sampling system. These data verify that the CO₂ meter is accurately measuring the atmospheric CO₂ concentration, which is approximately 300 ppm. The next series of data from approximately 0.20 to 0.40 hours were obtained with the CO₂ meter connected to the soil gas sampling system, which had not yet been connected to the wellhead. These measurements are also approximately 300 ppm, indicating that the CO₂ meter is correctly measuring the concentrations of CO₂ in the air moving through the soil-gas sampling system. The soil-gas sampling system is then connected to the wellhead and the soil gas is purged from the system and well bore. As the soil gas displaces the atmospheric air in the system, the CO₂ concentrations rise until near steady state conditions are achieved. After the CO₂ concentration have reached a near steady state condition, the system was disconnected from the well head and the meter allowed to measure CO₂ concentrations in atmospheric air, again to show that the system is functioning properly. The CO₂ meter calibration was checked and found to be within the acceptable calibration range following the completion of the measurements.

Figure 4-1. A schematic diagram showing the CO₂ concentration measurement system and process.

The measurements of soil gas CO₂ concentrations made under the near steady state conditions were averaged to determine the CO₂ concentration for the depth interval. The measurements (see Table 4-12) used to determine the average CO₂ concentrations were typically within 3% of the average, which shows a high degree of repeatability for the measurements.

The results show a significant variation in the CO₂ concentration with depth ranging from 4,700 ppm to 21,000 ppm. The average CO₂ concentration measured in the subsurface is 11,200 ppm. These values are two to three orders of magnitude greater than atmospheric CO₂ concentrations, which are typically around 300 ppm. There is a marked decrease in the soil gas CO₂ within the Plio-Pleistocene formation, which is characterized by a calcareous cementation of the sediments.

4.1.6.1 Calculated pH Values

The pH of the soil moisture was calculated using the measured CO₂ concentrations and the alkalinity of the sediment-water extracts from Equation 2-6. The results are presented in Table 4-12 and shown graphically on Plate 3. The calculated pH values range from slightly more than 6 to slightly less than 7 and are generally one pH unit lower than the laboratory measurements. This confirms that the pH measurement of soil moisture must not be taken after the samples are exposed to atmospheric CO₂ pressures.

The plot shown in Figure 4-2 clearly shows the importance of in situ pH measurements. The blue line is a plot of uranium sorption as a function of pH. This curve was generated using MINEQL+ V4.5, the model parameters used were: $\text{Log pCO}_2 = -2.13$, Ionic Strength = 2.10×10^{-3} , $\text{UO}_2^{+2} = 3.7 \times 10^{-6}$ mol/L, and Total $\text{Fe}^{+3} = 1 \times 10^{-3}$ mol/L. The red line shows the frequency distribution of the in situ pH values determined using the CO_2 data and the green line shows the frequency distribution of the laboratory measurements. The uranium sorption in the range of the pH values determined using the CO_2 data ranges from 60% to 80%, while the uranium sorption in the range of the pH values measured in the laboratory is less than 10%.

Figure 4-2. Plot of uranium sorption and frequency of pH values from CO_2 data and laboratory measurements.

4.2 PRELIMINARY GEOCHEMICAL MODELING

A preliminary geochemical model was compiled, and a sensitivity analysis was conducted. The purpose for the sensitivity analysis was to evaluate the limitations of the available data and determine which geochemical model parameters are relevant to this study in terms of adsorption of uranium to the soils. The parameters that were investigated in the sensitivity analysis include the surface complexation structural model, the concentration of both surface sites and UO_2^{+2} in solution, the variations in the CO_2 concentration, and the effects of additional ions in solution. The results from the sensitivity analysis are summarized in a separate report titled *Hanford Uranium Mobility Geochemical Modeling: Sensitivity Analysis* issued May 17, 2002 (MSE, 2002b) and in Section 4.2.1 of this report.

Based on the results from the sensitivity analysis, the first iteration of the geochemical model and description of the uranium transport in the unsaturated and saturated soils for this project was developed during FY02. The model took into account variations in the types of soils, soil chemistry, and groundwater chemistry at the site.

4.2.1 Sensitivity Analysis for Uranium Sorption

This phase of geochemical modeling was conducted to examine how MINEQL+ handles large variations in input parameters and works with an expanded and refined thermodynamic database. MSE investigated the sensitivity of UO_2^{+2} adsorption, as a function of pH, to the following parameters:

- changes in the sorption resulting from changes in the concentration of surface sites;
- affect of UO_2^{+2} concentrations in solution within a broad range of concentrations (3.7×10^{-7} mol/L to 3.7 mol/L) that include those observed for current conditions. Most of the sensitivity analysis was run using a concentration of 3.7×10^{-6} mol/L;
- effect of the CO_2 concentration on sorption; and
- effects of additional ions in solution such as Ca^{+2} , K^+ , Mg^{+2} , Na^+ , Al^{+3} , Cl^- , F^- , NO_3^- , PO_4^{-3} , and SO_4^{-2} .

The results of the sensitivity analysis were previously reported in *Hanford Uranium Mobility Geochemical Modeling: Sensitivity Analysis* (MSE, 2002a).

In general, the sensitivity analysis indicated UO_2^{+2} adsorption is proportional to both the surface site density and the concentration of UO_2^{+2} in solution and inversely proportional to the CO_2 concentration in the soils. The addition of Mg^{+2} , F^- , PO_4^{-3} , and SO_4^{-2} to the system causes a decrease in UO_2^{+2} adsorption. The decrease in UO_2^{+2} adsorption is more gradual as F^- or SO_4^{-2} is added. In contrast, UO_2^{+2} adsorption is drastically decreased because of a slight concentration change of either Mg^{+2} or PO_4^{-3} in the system. The remaining ions (Ca^{+2} , K^+ , Na^+ , Al^{+3} , Cl^- , and NO_3^-) did not significantly affect UO_2^{+2} adsorption over the range of concentrations modeled.

4.2.1.1 Surface Site Concentration

MINEQL+ allows a finite number of surface sites for adsorption modeling. To examine the sensitivity of the UO_2^{+2} adsorption to surface site concentration, a series of sorption simulations were run. The simulations used a constant UO_2^{+2} concentration and varied the concentration of $\equiv\text{FeOH}$ sorption sites. The model used for the sensitivity analysis calculates the concentration of $\equiv\text{FeOH}$ sorption sites from the total iron concentration. For this portion of the sensitivity analysis, the total iron concentrations ranged from 1 mol/L to 10^{-4} mol/L.

As the number of available surface sites decreases in the soil structure, it follows that the amount of UO_2^{+2} that can be adsorbed onto the soil will also decrease. This is observed in the results shown in Figure 4-3 where the adsorption is plotted for the range of iron concentrations.

Figure 4-3. UO_2^{+2} adsorption versus total Fe concentration and at a constant pH and constant UO_2^{+2} concentration. Results were generated using the Dzombak and Morel $\equiv\text{FeOH}$ surface complexation model. The UO_2^{+2} concentration used was $3.7 \times 10^{-6} \text{ mol/L}$, the ionic strength was $2.1 \times 10^{-3} \text{ mol/L}$, and the $\text{Log } p\text{CO}_2$ was -2.13 .

As the concentration of sorption sites decreases, the percentage of the total uranium adsorbed to the soil also decreases and the pH window that sorption will occur also becomes smaller.

4.2.1.2 UO_2^{+2} Concentrations in Solution

Another important observation that can be made relevant to the ratio of uranium in solution to the number of sorption sites is shown in Figure 4-4, which is a plot of the of UO_2^{+2} adsorption against the total UO_2^{+2} concentration at a constant pH and total Fe(III).

Figure 4-4. UO_2^{+2} adsorption versus total UO_2^{+2} concentration at constant pH and constant total Fe(III). Results were generated using the Dzombak and Morel $\equiv\text{FeOH}$ surface complexation model. The total Fe(III) concentration used was 1×10^{-3} mol/L, the ionic strength was 2.1×10^{-3} mol/L, and the $\text{Log } p\text{CO}_2$ was -2.13 .

Figure 4-4 shows that the ratio of adsorbed UO_2^{+2} to total UO_2^{+2} is not constant over the range of total UO_2^{+2} concentrations shown. This is most likely due to all of the available sorption sites being occupied by UO_2^{+2} and not to changes in the UO_2^{+2} complexation affinity.

4.2.1.3 Effect of CO_2 Concentrations on Sorption

As previously indicated, UO_2^{+2} is most mobile at the low and high pH ranges and tends to be adsorbed if the pH is near neutral. Since pH is influenced by the concentration of CO_2 in the air (Langmuir, 1997), changes in CO_2 concentration will affect the adsorption of UO_2^{+2} . Figure 4-5 is a plot showing the effect of the CO_2 concentration on UO_2^{+2} adsorption over CO_2 concentrations ranging from 300 ppm ($\text{log } p\text{CO}_2 = -3.5$) to 30,000 ppm ($\text{log } p\text{CO}_2 = -1.5$), which are representative of the concentrations measured in borehole 299-W19-43.

Figure 4-5. Effects of Log pCO₂ values on total percent UO₂⁺² adsorption as a function of pH. Results were generated using the Dzombak and Morel $\equiv\text{FeOH}$ surface complexation model. The total Fe(III) concentration used was 1×10^{-3} mol/L, the concentration of UO₂⁺² was 3.7×10^{-6} mol/L, and the ionic strength was 2.1×10^{-3} mol/L.

As the concentration of CO₂ increases, the percentage of the total uranium adsorbed to the soil decreases and the pH window that sorption will occur also becomes smaller.

In addition to affecting the solution pH, the dissolved CO₂ forms carbonate complexes with UO₂⁺². The occurrence and abundance of these complexes depends on both the pH and alkalinity of the solution, which are typically functions of the dissolved CO₂. These uranyl-carbonate complexes are orders of magnitude more soluble than UO₂⁺²; thus decreasing the adsorption of uranium to the soil. Important uranyl-carbonate complexes include UO₂CO₃⁰, UO₂(CO₃)₂⁻², and UO₂(CO₃)₃⁻⁴.

4.2.1.4 Effects of Ions in Solution

The ionic species that significantly affected UO_2^{+2} adsorption based on the sensitivity analysis included: Mg^{+2} , F^- , PO_4^{-3} , and SO_4^{-2} . The results of the simulations in which the concentrations of these ions were varied over a range of concentrations are shown in the following plots (Figure 4-6 through Figure 4-9). The range of concentrations represents those measured in both the Columbia River water and in the Hanford groundwater.

Figure 4-6. Effects on total percent UO_2^{+2} adsorption from the addition of Mg^{+2} to the solution. Results were generated using the Dzombak and Morel $\equiv\text{FeOH}$ surface complexation model. The total Fe(III) concentration used was 1×10^{-3} mol/L, the concentration of UO_2^{+2} was 3.7×10^{-6} mol/L, the ionic strength was 2.1×10^{-3} mol/L, and the Log $p\text{CO}_2$ was -2.13 .

Figure 4-6 shows the percent of UO_2^{+2} adsorbed decreasing as the concentration of Mg^{+2} increases. There is a decrease in UO_2^{+2} adsorption of approximately 10% between the 1×10^{-5} mol/L and 1×10^{-4} mol/L Mg^{+2} concentrations. UO_2^{+2} adsorption drastically decreases from about 70% down to almost 0% between the 1×10^{-4} mol/L and 1×10^{-3} mol/L Mg^{+2} concentrations. The decrease in UO_2^{+2} adsorption is a result of the Mg^{+2} competing for the $\equiv\text{FeOH}$ surface sites.

Figure 4-7. Effects on total percent UO_2^{+2} adsorption from the addition of F^- to the solution. Results were generated using the Dzombak and Morel $\equiv FeOH$ surface complexation model. The total $Fe(III)$ concentration used was 1×10^{-3} mol/L, the concentration of UO_2^{+2} was 3.7×10^{-6} mol/L, the ionic strength was 2.1×10^{-3} mol/L, and the $\text{Log } pCO_2$ was -2.13 .

Results shown on Figure 4-7 indicate that the presence of F^- in the system can affect the adsorption of UO_2^{+2} . When F^- is added to the system, UO_2^{+2} adsorption decreases and the low-pH UO_2^{+2} adsorption edge shifts to the right, toward higher pH values. Modeling results indicate that uranyl-fluoride species $UO_2F_3^-$, $UO_2F_2(aq)$, and UO_2F^+ are present in the lower pH range, preventing the UO_2^{+2} from adsorbing.

Figure 4-8. Effects on total percent UO_2^{+2} adsorption from the addition of PO_4^{-3} to the solution. Results were generated using the Dzombak and Morel $\equiv\text{FeOH}$ surface complexation model. The total Fe(III) concentration used was 1×10^{-3} mol/L, the concentration of UO_2^{+2} was 3.7×10^{-6} mol/L, the ionic strength was 2.1×10^{-3} mol/L, and the Log $p\text{CO}_2$ was -2.13 .

The modeling results shown in Figure 4-8 suggest that the presence of PO_4^{-3} in the system can significantly affect the adsorption of UO_2^{+2} . The adsorption of UO_2^{+2} drastically decreases from about 85% down to almost 0% between the 1×10^{-5} mol/L and 1×10^{-4} mol/L PO_4^{-3} . The results also indicate that uranyl-phosphate species ($\text{UO}_2\text{H}_2\text{PO}_4^+$, $\text{UO}_2(\text{HPO}_4)_2^{-2}$, $\text{UO}_2(\text{H}_2\text{PO}_4)_2(\text{aq})$, $\text{UO}_2(\text{H}_2\text{PO}_4)_3^-$, and $\text{UO}_2(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)^+$) are present in the lower pH range, which act to keep the UO_2^{+2} in solution.

Figure 4-9. Effects on total percent UO_2^{+2} adsorption from the addition of SO_4^{-2} to the solution. Results were generated using the Dzombak and Morel $\equiv\text{FeOH}$ surface complexation model. The total Fe(III) concentration used was 1×10^{-3} mol/L, the concentration of UO_2^{+2} was 3.7×10^{-6} mol/L, the ionic strength was 2.1×10^{-3} mol/L, and the Log $p\text{CO}_2$ was -2.13 .

Figure 4-9 shows that the presence of SO_4^{-2} in the system can affect the adsorption of UO_2^{+2} . When SO_4^{-2} is added to the system, UO_2^{+2} adsorption decreases and the low-pH UO_2^{+2} adsorption edge shifts to the right, toward higher pH values. Modeling results indicate that the formation of uranyl-hydroxide, uranyl-sulfate, and uranyl-carbonate species is the primary cause of the decrease in UO_2^{+2} adsorption.

4.3 INITIAL GEOCHEMICAL MODEL CALIBRATION

The model calibration was completed through a series of batch tests to determine the amount of uranium adsorption to the Hanford soils over a range of pH values. The results of the batch testing were used to optimize the geochemical model parameters. The batch tests were conducted in an atmosphere with a controlled CO_2 concentration.

Water obtained from the Columbia River upstream of the Vernita Bridge on the north side of the Hanford Site was used for the batch testing. This was done for two reasons: (1) the process waters that were discharged to the cribs were originally from the Columbia River, and (2) the use of Columbia River water

also eliminated any issues associated with using groundwater from the Hanford Site due to contamination and focused the efforts of the study on conducting the batch tests.

The soil samples collected during the FY01 drilling activities were transferred to MSE for use in the model calibration batch testing and for later use in the model validation study. The batch testing for the model calibration was conducted at the Mike Mansfield Advanced Technology Center in Butte, Montana. The model calibration batch testing results are further detailed in the FY02 status report (MSE, 2002a).

4.3.1 Batch Tests for Model Calibration

The batch tests to compare the measured sorption of UO_2^{+2} to the adsorption predicted by the geochemical model were completed according to the procedures outlined in *Calibration Plan for Geochemical Model Describing Uranium Transport in the Unsaturated and Saturated Sediments at the 200 West Area of the Department of Energy Hanford Site, Washington* (MSE, 2002b).

4.3.1.1 Batch Test Solid Phase

The calibration batch tests were completed using five types of soil taken from the core samples acquired from well 299-W19-43 on the Hanford site. The soil samples are described in Table 4-13.

Table 4-13. Summary of soil samples used in model calibration batch tests.

Sample	Core	Formation	Description
1	MSE-CORE-101B	Hanford Unit 1	Light brown gray (2.5Y 6/2) to grayish brown (2.5Y 5/2); Medium to coarse grained sand; Subrounded; 40-50% basalt; Quartz in dominant with minor amounts of plagioclase and feldspar and trace pyrite; no visual reaction with HCl; Loose, dry soil; 2-3% magnetite
2	MSE-CORE-104B	Hanford Unit 2	Pale yellow (2.5Y 7/3); very fine to fine grained sand; Rounded to subrounded; 5% basalt; Quartz is dominant; Reddish-orange staining; Slight reaction with HCl; Little to no moisture; 1% magnetite
3	MSE-CORE-106B	Hanford Unit 2	Very pale brown (10YR 7/3 to 10YR 7/4); Very fine grained silty sand; Rounded to subrounded; 1-2% basalt; Quartz is dominant; Slight to moderate reaction with HCl; Loose to slightly cemented; Little to no moisture; Trace amount of magnetite
4	MSE-CORE-112B	Plio-Pleistocene Caliche	Pale yellow (2.5Y 8/3 to 2.5T 8/4); Silt to very fine grained sand; Subrounded; <1-1% basalt; some quartz; Carbonate present; strong reaction with HCl; Highly cemented but has high transmissivity; trace amount of magnetite.
5	MSE-CORE-119B	Ringold Upper Gravels	Gravel with silty-sand matrix; Matrix is: Light yellow brown (2.5Y 6/3); Silt to very fine grained sand; subrounded; <1-1% basalt; some quartz; No visible reaction with HCl; Loose; Trace amount of magnetite

4.3.1.2 Batch Test Aqueous Phase

The calibration batch tests were completed using Columbia River Water. The water was spiked with uranyl-nitrate at two concentrations (Low Uranium and High Uranium) to produce the stock solutions used in the initial batch testing. The concentrations were chosen based on the range of dissolved uranium reported for the 200-UP-1 Operable Unit (EPA, 1997). Aliquots of each stock solution were taken and the pH adjusted to obtain seven laboratory solutions ranging in pH from 3 to 9.

The concentration of uranium in the stock solutions was measured in the laboratory and used to calculate the initial concentration of uranium in the soil/water mixtures (see Table 4-14).

Table 4-14. Measured uranium concentrations in initial batch test solutions.

		Low Uranium Stock Solution	High Uranium Stock Solution
Stock Solutions	mg/L	0.149	1.28
	mol/L	6.26E-07	5.38E-06
Soil/Water Mixtures	mg/L	0.0745	0.64
	mol/L	3.13E-07	2.69E-06

4.3.1.3 Batch Test Gas Phase

The batch testing was conducted in a CO₂ controlled atmosphere to simulate the CO₂ concentrations measured during the installation of well 299-W19-43. The CO₂ concentrations selected for the batch testing included 5,000 ppm, 10,000 ppm, and 20,000 ppm. These CO₂ concentrations represented the range of concentrations measured for the samples selected for the batch testing. During the batch testing, the CO₂ concentrations were monitored to ensure the testing conditions were representative of the selected subsurface conditions and to provide data for later geochemical modeling efforts. The measured CO₂ concentrations during the batch testing are presented in Figure 4-10. The average values measured during the batch testing are presented in Table 4-15.

Table 4-15. Subsurface and batch test CO₂ concentrations.

Sample Description	Approximate Depth (ft)	Subsurface CO ₂ Concentration (ppm)	Average Batch Test CO ₂ Concentration (ppm)
MSE-CORE-101B	21.5	3,916	4,657
MSE-CORE-104B	111.3	17,806	20,358
MSE-CORE-106B	171.5	8,783	10,285
MSE-CORE-112B	195.8	7,773	10,285
MSE-CORE-119B	231.4	5,771	4,657

Figure 4-10. CO₂ monitoring measurements acquired during the calibration batch tests.

4.3.1.4 Batch Testing

The batch tests were conducted in a glove box to provide the CO₂ concentration control. A picture of the laboratory setup is shown in Figure 4-11. For each batch test, a small quantity of soil was placed in a test tube (approximately 5 grams of soil) and mixed, using a roller table, with Columbia River water (approximately 25 mL) for one day. This was done to equilibrate the soil with the water. The pH adjusted stock solution water (approximately 25 mL) was added to the pre-equilibrated soil/water mixture. The test tubes were gently agitated using the roller table for 2 hours per day for three days. Between rollings, the soil/water mixtures were left open to the glove box atmosphere to equilibrate with the CO₂. The pH of the solution was measured and adjusted if necessary between each rolling. The pH adjustments were made using HCl and NaOH solutions. After the third rolling, the mixtures were centrifuged and final pH measurements were made. From each soil/water mixture, a subsample of water was extracted. These subsamples were filtered and preserved for laboratory analysis.

Figure 4-11. Batch testing laboratory setup at MSE.

Quality control during the batch testing followed the specifications outlined in the calibration test plan. This included duplicate samples; blank samples with water only; and blank samples of spiked water.

4.3.2 Geochemical Modeling of Batch Tests

The initial geochemical model was designed to simulate conditions of the batch testing. The model parameters for the initial geochemical model were obtained from laboratory analyses, measurements made during the batch tests, and relevant literature values. Laboratory analytical data included concentrations of ionic species in the Columbia River water and the total extractable iron in each soil type. CO_2 concentrations measured during the model calibration batch testing were also used in the initial modeling. Parameters taken from literature included thermodynamic constants, the surface area of the primary sorbent (iron-hydroxide), and the surface site density for the sorbent.

4.3.2.1 Aqueous Component Concentrations

Concentrations of the ions present in the Columbia River water were determined through laboratory analysis. The aqueous components analyzed for and the corresponding concentrations used in the initial geochemical model are shown in Table 4-16.

Table 4-16. Aqueous component concentrations used in the initial geochemical model.

Aqueous Components	Concentration (mg/L)	Concentration (mol/L)
Al ⁺³	<i>NON DETECT</i>	
Ca ⁺²	21	5.24E-04
Cl ⁻	2	5.64E-05
F ⁻	0.1	5.26E-06
Fe ⁺³	<i>NON DETECT</i>	
K ⁺	1	2.56E-05
Mg ⁺²	5	2.06E-04
Na ⁺	3	1.30E-04
NO ₃ ⁻	0.21	1.50E-05
PO ₄ ⁻³	0.03	3.16E-07
Si(OH) ₄ (as Si)	2.7	9.61E-05
SO ₄ ⁻²	13	1.35E-04
Zn ⁺²	0.03	4.59E-07

The ionic strength used in the modeling was calculated from the aqueous components and corresponding concentrations. The ionic strength (*I*) of the solution was calculated using the Davies equation:

$$I = \frac{1}{2} \sum (m_i z_i^2) \quad (4-2)$$

where *I* is in molal or molar units, *m_i* is the concentration of ion *i*, and *z_i* is the charge of ion *i*. From this, the ionic strength of the solution was calculated to be 1.85x10⁻³ molar.

For each soil sample, an initial high (0.64 mg/L) and low (0.0745 mg/L) uranium concentration were modeled. These were the concentrations of the soil/water mixtures from the batch testing.

4.3.2.2 Carbon Dioxide Concentrations

As previously discussed in Section 4.3.1.3, the CO₂ concentrations were measured during the batch testing. The average concentrations of the three target CO₂ concentrations (see Table 4-15) for the batch testing were included in the model as the log of the partial pressure, in atmospheres, of CO₂.

4.3.2.3 Thermodynamic Data

Equilibrium constants, enthalpy values, and stoichiometric coefficients of the aqueous complexes form the basis of the geochemical model. The thermodynamic database used in the geochemical modeling efforts was derived mainly from the chemical equilibrium modeling program MINEQL+© v. 4.5. In addition to the thermodynamic data included in MINEQL+© v. 4.5, MSE compiled thermodynamic data using information from professionals and recent studies in uranium adsorption. Sources for the thermodynamic database include:

- MINTEQA2 v4.02 (Allison et al., 1991) with updated uranium thermodynamic data;
- *Surface Complexation Modeling: Hydrous Ferric Oxide* (Dzombak and Morel, 1990);
- *Uranium (VI) Interactions with Mineral Surfaces: Controlling Factors and Surface Complexation Modeling* (Payne, 1999);

- *Uranium (VI) Transport Modeling: Geochemical data and Submodels* (Tripathi, 1983);
- *Adsorption of Uranyl Onto Ferric Oxyhydroxides: Application of the Surface Complexation Site-Binding Model* (Hsi and Langmuir, 1985);
- *NIST Critical Stability Constants of Metal Complexes Database, NIST Standard Reference Database 46* (Smith and Martell, 1993);
- *Mixed-Metal Hydroxycarboxylic Acid Complexes - Formation Constants of U(VI) with Fe(III), Al(III), In(III), and Cu(II)* (Manzurola et al., 1989);
- *The Hydrolysis of Cations* (Baes and Mesmer, 1976);
- *Critical Stability Constants, Volume 4: Inorganic Complexes* (Smith and Martell, 1976); and
- *U(VI) Adsorption to Heterogeneous Subsurface Media: Application of a Surface Complexation Model* (Barnett et al., 2002).

4.3.2.4 Surface Complexation Sorbent Data

The surface complexation sorbent data specifically relates to the description of the sorbent(s) considered in the geochemical model. These data include the sorbent type and structure, surface area, and site density. Iron-hydroxide minerals are being considered the main sorbent for the geochemical modeling.

As previously discussed, studies indicate that iron-hydroxide surface sites ($\equiv\text{FeOH}$) dominate UO_2^{+2} adsorption. Using the CBD analytical results, previously discussed in Section 4.1.5, and the quantities of soil and groundwater used in the calibration batch samples, the concentrations of adsorbing solid ($\equiv\text{FeOH}$) were calculated for each soil sample and are presented in Table 4-17.

Table 4-17. Solid $\equiv\text{FeOH}$ concentration values for geochemical model.

Sample Description	Approximate Depth (ft)	Grams of $\equiv\text{FeOH}$ per Kilogram of Soil (CBD)	Mass (g) of Soil in Batch Sample	Volume (mL) of Groundwater in Batch Sample	Adsorbing Solid ($\equiv\text{FeOH}$) Concentration (g/L)
MSE-CORE-101B	21.5	1.66	5	54	0.154
MSE-CORE-104B	111.3	2.98	5	54	0.276
MSE-CORE-106B	171.5	3.76	5	54	0.348
MSE-CORE-112B	195.8	1.64	5	54	0.152
MSE-CORE-119B	231.4	3.85	5	54	0.356

The structure of the sorbent site may be described as either monodentate or bidentate. The terms monodentate and bidentate, when used to describe surface complexation structures, indicate the behavior of the surface in terms of the surface site chemistry (Hiemstra and Riemsdijk, 1998). A monodentate structure is one in which the surface site is treated as a point charge. A bidentate structure treats the site as a distribution of charges, and thus not all of the binding energy that might be available for a point charge is available in a bidentate structure. The bidentate structure results in increased competition for the surface site by the UO_2^{+2} ion with other ions in solution. At lower pH values, there is an increase in the number of H^+ ions in solution, resulting in less sorption of the uranium at lower pH values. Likewise, at higher pH values, there are fewer surface sites available, again resulting in less sorption of uranium. For the geochemical model, the structure of UO_2^{+2} adsorption to $\equiv\text{FeOH}$ sorption site is considered a bidentate one. Several sources have indicated, through laboratory analysis, that a bidentate structure is more likely than a monodentate one (Langmuir, 1997; Hiemstra and Riemsdijk, 1998; and Payne, 1999).

The initial geochemical model followed the $\equiv\text{FeOH}$ diffuse layer model described by Dzombak and Morel (1990). The specific surface area of the $\equiv\text{FeOH}$ sorbent was modeled as $600 \text{ m}^2/\text{g}$. The model also assumes two types of sorbing sites (strong, high affinity and weak, low affinity). The site densities of the

strong and weak sites were 0.005 moles of sites per mole of iron and 0.2 moles per sites per mole of iron, respectively.

4.3.2.5 Surface Complexation Reactions

As discussed in Section 4.3.2.3, thermodynamic data for the aqueous reactions were compiled from numerous sources. Thermodynamic constants for the surface complexation reactions describing UO_2^{+2} adsorption to $\equiv FeOH$ sites were also obtained from these sources. For the initial geochemical modeling efforts, only bidentate UO_2^{+2} and uranyl-carbonate surface complexation reactions with strong and weak adsorption sites were considered. The reactions and corresponding thermodynamic constants were:

Additional UO_2^{+2} surface complexation reactions considered for the geochemical modeling efforts include:

4.3.3 Initial Geochemical Modeling of the Batch Tests

The results of the initial geochemical model as compared to the results from the batch testing are presented in this section. The results are presented as plots of the percent of uranium adsorbed as a function of the pH under which the adsorption occurred for both the model predictions and observed data from the batch tests. The goodness-of-fit between the observed and predicted UO_2^{+2} adsorption data was evaluated quantitatively and qualitatively.

The goodness-of-fit between the results was determined by calculating the root mean squared error (RMSE) according to:

$$RMSE = \left[\frac{1}{(n_d - n_p)} \sum_{i=1}^{n_d} \left(\frac{C - C'}{C_o} \right)^2 \right]^{1/2} \quad (4-3)$$

Where: n_d is the number of data points, n_p is the number of adjustable parameters, C is the measured concentration, C' is the predicted concentration, and C_o is the initial concentration. The RMSE is a measure of the error between predicted and measured values expressed as a function of the initial concentration.

4.3.3.1 Batch Test Results

Final uranium concentrations in the batch test samples were measured in the laboratory and the resulting percentages of adsorbed uranium were calculated. Table 4-18 summarizes the data from the batch testing.

Table 4-18. Results of uranium adsorption batch tests.

	Low Uranium Stock Solution			High Uranium Stock Solution		
	pH Measured	U Concentration (mg/L) in Solution	% Adsorbed to Soil	pH Measured	U Concentration (mg/L) in Solution	% Adsorbed to Soil
MSE-CORE-101B	5.50	0.009	87.9	5.99	0.2	68.8
	5.94	0.034	54.4	6.19	0.303	52.7
	6.20	0.029	61.1	6.37	0.432	32.5
	6.63	0.067	10.1	6.87	0.571	10.8
	7.39	0.085	<i>-14.1</i>	7.58	0.691	<i>-8.0</i>
	7.75	0.085	<i>-14.1</i>	7.81	0.672	<i>-5.0</i>
	8.39	0.088	<i>-18.1</i>	8.31	0.646	<i>-0.9</i>
MSE-CORE-104B	6.02	0.028	62.4	6.17	0.405	36.7
	6.15	0.041	45.0	6.27	0.467	27.0
	6.38	0.018	75.8	6.36	0.449	29.8
	6.64	0.039	47.7	6.96	1.12	<i>-75.0</i>
	7.33	0.09	<i>-20.8</i>	7.26	1.42	<i>-121.9</i>
	7.97	0.104	<i>-39.6</i>	7.51	1.5	<i>-134.4</i>
	8.78	0.101	<i>-35.6</i>	8.07	0.735	<i>-14.8</i>
MSE-CORE-106B	5.28	0.011	85.2	5.36	0.218	65.9
	5.76	0.02	73.2	5.89	0.363	43.3
	6.18	0.01	86.6	6.40	0.53	17.2
	6.61	0.053	28.9	6.48	0.503	21.4
	7.39	0.08	<i>-7.4</i>	7.38	0.634	0.9
	7.94	0.088	<i>-18.1</i>	7.97	0.674	<i>-5.3</i>
	8.14	0.095	<i>-27.5</i>	9.01	0.682	<i>-6.6</i>
MSE-CORE-112B	6.28	0.084	<i>-12.8</i>	5.98	0.613	4.2
	6.46	0.076	<i>-2.0</i>	6.26	0.493	23.0
	6.45	0.04	46.3	6.32	0.475	25.8
	6.86	0.056	24.8	6.74	0.392	38.8
	7.47	0.054	27.5	7.45	0.444	30.6
	7.34	0.071	4.7	7.67	0.422	34.1
	8.55	0.115	<i>-54.4</i>	8.19	0.503	21.4
MSE-CORE-119B	3.90	0.014	81.2	4.76	0.139	78.3
	4.52	0.006	91.9	4.76	0.062	90.3
	5.54	0.003	96.0	5.54	0.031	95.2
	6.34	0.007	90.6	6.35	0.081	87.3
	7.17	0.051	31.5	7.15	0.503	21.4
	8.32	0.086	<i>-15.4</i>	7.56	0.574	10.3
	8.79	0.086	<i>-15.4</i>	8.71	0.634	0.9

Values in italics were assumed 0% for comparison to modeled values.

The negative values shown in Table 4-18 indicate that more uranium was in solution at the completion of the batch test than what was initially in the stock solution at the onset of the batch tests. This may be a

result of uranium initially in the soil desorbing during the batch testing. Laboratory error is also a possible reason for this discrepancy.

4.3.3.2 Initial Geochemical Modeling Results

The initial conditions of the soil/water mixtures for each batch test were modeled to predict the UO_2^{+2} adsorption. The analytical data from the batch tests were then compared to the predicted data from the geochemical model. The following figures (4-12 through 4-16) illustrate the results of the initial geochemical model iterations and the laboratory batch tests.

Discrepancies between the model and laboratory results may be attributed to several factors including over/under estimation of available adsorption sites, errors in thermodynamic constants, and inclusion and/or exclusion of specific chemical reactions. While the RMSE values for the models indicate poor agreement between the modeled and observed values for adsorption, the general shape of the modeled and observed sorption curves in most cases is promising.

Figure 4-12. Geochemical modeling and batch test results for MSE-CORE-101B. RMSE between the model and laboratory values was 7.83 for the high uranium concentration and 7.61 for the low uranium concentration.

Figure 4-13. Geochemical modeling and batch test results for MSE-CORE-104B. RMSE between the model and laboratory values was 8.90 for the high uranium concentration and 6.66 for the low uranium concentration.

Figure 4-14. Geochemical modeling and batch test results for MSE-CORE-106B. RMSE between the model and laboratory values was 7.87 for the high uranium concentration and 6.80 for the low uranium concentration.

Figure 4-15. Geochemical modeling and batch test results for MSE-CORE-112B. RMSE between the model and laboratory values was 7.43 for the high uranium concentration and 8.70 for the low uranium concentration.

Figure 4-16. Geochemical modeling and batch test results for MSE-CORE-119B. RMSE between the model and laboratory values was 5.43 for the high uranium concentration and 3.46 for the low uranium concentration.

4.4 U-PLANT AGGREGATE AREA WASTE DISPOSAL INVENTORY

Information from previous reports and documentation from the Hanford Site pertaining to the inventory of the wastes disposed of in the 216-U1/U2 Cribs was compiled and reviewed. In addition, the reviews helped to determine and/or estimate the pH and chemistry of the waste stream discharged to the cribs. This information was summarized in a separate report (MSE, 2002c). This report provided uranium inventory information for the U-Plant Aggregate Area, focusing on uranium species stripped from fission products contained in the Bismuth-Phosphate (BP) process wastes in the 200 West Area.

5. FISCAL YEAR 2003 ACTIVITIES

The primary FY03 project activities initiated and or completed include an analysis of uranium isotope ratios for soil samples that were obtained from various boreholes surrounding the site; completing the geochemical model calibration; and validating the geochemical model.

5.1 URANIUM ISOTOPE RATIO INVESTIGATION

The uranium isotope analysis was completed in an effort to understand the nature of the uranium in the caliche or Plio-Pleistocene soils surrounding the site. This was undertaken because some soils used for the batch testing, particularly the Plio-Pleistocene soils, contained measurable quantities of uranium, and it was important to know if this uranium was associated with the waste disposal practices at the site or if it was a naturally occurring uranium.

This informal study was based on the ratios of U^{234} , U^{235} , and U^{238} in the soils. For naturally occurring uranium, U^{234} is generally around 0.0054% by weight of the total uranium in the soils while the percentage of U^{235} is 0.7110% by weight and U^{238} is 99.2830% by weight (Lide, 1990). This is in contrast to enriched uranium, which has a higher percentage of U^{235} by weight. If higher percentages of U^{235} were detected in the soils over that found in naturally occurring uranium, it may suggest that the uranium was from the discharges to the cribs. This is based on the assumption that uranium discharged to the cribs would contain slightly elevated levels of U^{235} . For control, uranium isotope ratios for soils from the same stratigraphic unit, but located within the White Bluffs area northeast of the site, were also measured. It is believed that any uranium in the control soils would be naturally occurring.

The investigation consisted of leaching uranium from the soils and then analyzing the uranium isotopes in the leachate to determine the isotope ratio. The analysis measured the different emission energies within the uranium spectrum and the results were reported in picoCuries per liter (pCi/L) of leachate solution. The reported results could not be directly converted to mass; however, the count ratios can be compared to determine if the uranium found in the samples is similar to the control data from White Bluffs.

Samples from wells surrounding the U1/U2 cribs were used for the study. The locations of these wells are shown on Figure 5-1. The samples were obtained from the Hanford Core Library and shipped to MSE by PNNL. The soils were leached using deionized water and hydrochloric acid for a period of several days. The mass of soil, volume of water, volume of acid used, and the final pH of the soil and leachate mixture were all measured and recorded during the leaching process. The leachate was shipped to a laboratory for the uranium isotope analysis. The wells that samples were obtained from and the relative percentages of the total activity for each of the three uranium isotopes (i.e., U^{234} , U^{235} , U^{238}) are shown in Table 5-1.

The percentages of U^{234} , U^{235} , and U^{238} for all of the soils excluding the soils from the 167- to 170- ft depth in well 299-W19-15, as indicated by the emissions, were within 1 standard deviation of the average values measured. This suggests that all of the uranium contained in the soil samples, with the exception of the soil from the 167- to 170- ft depth in well 299-W19-15 (shown in bold italics), is similar in composition to the uranium from the caliche unit sampled from the White Bluffs area. No additional work was completed with respect to these data; however, they will be considered in the final assessment of the conceptual model for the site.

Figure 5-1. Locations of wells from which uranium isotope soil samples were obtained.

Table 5-1. Uranium isotope data.

Well # and Sample Depth	Percentage (%) of Total Uranium Activity in Soils		
	U ²³⁴	U ²³⁵	U ²³⁸
299-W19-13 170'	52.7	1.9	45.5
299-W19-14 185'	50.6	3.8	45.6
299-W19-14 190'	42.2	2.4	55.3
299-W19-14 195'	43.9	3.1	52.9
299-W19-14 200'	51.5	2.1	46.4
299-W19-15 160' to 165'	48.4	1.8	49.8
299-W19-15 165' to 166'	50.3	2.0	47.7
299-W19-15 167' to 170'	86.1	4.6	9.3
299-W19-16 160' to 165'	47.7	2.5	49.8
299-W19-16 167' to 170'	48.3	2.0	49.7
299-W19-17 160' to 165'	49.4	1.5	49.1
299-W19-17 165' to 170'	48.5	3.5	48.0
299-W19-18 165' to 170'	52.9	2.0	45.1
299-W19-18 170' to 175'	46.2	5.1	48.7
299-W19-34A 187'	51.3	1.1	47.7
299-W19-34A 190'	50.7	1.9	47.4
299-W19-34A 195'	49.5	5.4	45.1
299-W19-95 165'	51.4	2.5	46.1
299-W19-95 169'	55.6	0	44.4
299-W19-97 165' to 167.5'	50.0	6.1	43.9
White Bluffs Caliche Sample	52	2	46

5.2 GEOCHEMICAL MODEL CALIBRATION AND VALIDATION

During FY03, additional laboratory batch tests were completed to address issues that were not resolved during the first round of calibration batch tests completed in FY02. The results of this effort increased the total number of samples used for model calibration, resulting in improved geochemical model parameter estimations. These results are discussed in detail in Section 5.2.3 of this report.

There were 416 batch tests completed for the additional calibration testing, which was completed using soils from 5 of the 7 geochemical horizons identified from the soil characterization and water obtained from the Columbia River upstream of the Vernita Bridge on the north side of the Hanford Site. These soils and waters were the same as those used for the initial model calibration batch tests. However, the additional batch tests, were open to the atmosphere and thus did not include effects from changes in the CO₂ pressure of the soil gases, as the initial batch test had. For the second set of batch tests, the decision not to conduct the batch test in a CO₂ controlled atmosphere was primarily due to logistics associated with the number of samples.

Each of the five soils were mixed with Columbia River water that was pH adjusted, with the pH ranging from 3 to 7. For each of these solutions, there was a group of batch tests (generally a triplicate) for dissolved metals analysis, individual analyses of nonmetals, and a series of quality assurance analyses.

The triplicate analyses of dissolved metals included aluminum, calcium, iron, magnesium, manganese, potassium, sodium, uranium, and silicon. The non-metals analyses included alkalinity, chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}). The quality assurance samples included samples of spiked water only for each pH, Columbia River water only at each pH, and Columbia River water and soil with no uranium at each pH.

The geochemical model validation was completed and a summary submitted with the milestone completion letter on September 30, 2003, to meet the FY03 milestone M3-02. The model validation followed the validation plan issued by MSE in March 2003, and is presented and discussed in Section 5.2.4 of this report. The model validation included a limited characterization of soils from two previously uncharacterized intervals from well 299-W19-43, modeling the uranium sorption expected for these intervals, and conducting a series of batch tests on these sediments determine the uranium sorption for comparison to the model results.

The geochemical model software, geochemical model input, geochemical model calibration, and geochemical model validation are presented in this section. MSE chose to use a chemical equilibrium model to calculate the partitioning of uranium between the soil and groundwater. This partitioning is based on the diffuse-layer surface complexation model and the assumption that the primary sorbent of U(VI) in the soils was iron. The affinity of the U(VI) to be adsorbed to the sorbing sites is a function of the ionic strength and pH of the solution, the U(VI) and carbonate concentrations in solution, and the sorbent surface area and site density.

5.2.1 Geochemical Model Software

For the geochemical model efforts, including the model calibration and validation, MSE used the software package MINEQL+[®] v. 4.5 (Schecher and McAvoy, 2001). MINEQL+[®] is a Windows[™]-based chemical equilibrium modeling system that was derived from the public domain code, MINTEQA2 (Allison et al., 1991). MINEQL (Westall et al., 1976) forms the numerical engine for MINEQL+. The database assembled in MINEQL+ is derived from several sources including MINTEQA2, MINEQL, and WATEQ4F (Ball and Nordstrom, 1991).

Chemical equilibrium models are designed to calculate the composition of dilute aqueous solutions or the mass distributions between dissolved, desorbed, and multiple solid phases under a variety of conditions (Allison et al., 1991). A set of chemical species are defined in the chemical equilibrium model based on an initial set of chemical components, which are determined from the chemical analysis of the aqueous solution of interest. The components can be considered the basic building blocks of the system (Schecher and McAvoy, 2001). Mass action expressions are then written in terms of component activities (equilibrium constants), which are typically contained in a database. The total mass for each component is calculated from the concentration of every species containing that component. The calculated total mass is then compared to the known input total mass for each component. The aqueous-phase equilibrium composition is that set of species concentrations that give a mass imbalance less than a predefined tolerance level.

Surface complexation, which considers the formation of solid-solution complexes, is handled in the chemical equilibrium model by treating the solid-solution complexes as species made up of a component or species in solution and a second component or species that exists as the solid phase. Equilibrium constants for the formation of the solid-solution complexes are treated similar to the equilibrium constants for aqueous complexes.

5.2.2 Geochemical Model Input

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. Equilibrium constants, enthalpy values, and stoichiometric coefficients are used to define these reactions. The thermodynamic database used in the geochemical model efforts was taken mainly from MINEQL+. In addition, MSE compiled thermodynamic data using information from professionals and recent studies on uranium adsorption. Sources for the thermodynamic database include: Barnett et al., 2002; Giammar, 2001; Schecher, 2001; Payne, 1999; Parkhurst and Appelo, 1999; Langmuir, 1997; Meinrath et al., 1996; Waite et al., 1994; Smith and Martell, 1993; Grenthe et al., 1992; Kramer-Schnabel et al., 1992; Sandino and Bruno, 1992; Silva, 1992; Allison et al., 1991; Choppin and Mathur, 1991; Dzombak and Morel, 1990; Bruno and Puigdomenech, 1989; Manzurola et al., 1989; Hsi and Langmuir, 1985; Tripathi, 1983; Baes and Mesmer, 1976; and Smith and Martell, 1976.

These sources were used primarily for determining the equilibrium constants for the aqueous, surface complexation and solid reactions at 25 °C and an ionic strength equal to zero. Enthalpy values were not critical because all modeling was performed assuming the systems were at 25 °C.

5.2.2.1 Model Components

“Model Components” are the cations and anions that are the basic building blocks of the chemical equilibrium model. These were chosen by taking into account the sensitivity of U(VI) sorption in the presence of the component (i.e., whether the component may compete for sorption sites and/or form aqueous components with U(VI) preventing it from sorbing), the initial and expected concentration of the component in the batch test solutions, and the initial and expected concentration of the components in the batch test soils. The cations selected as model components included: Al^{+3} , Ca^{+2} , Fe^{+2} , K^{+} , Mg^{+2} , Mn^{+3} , Na^{+} , Si^{+4} , and U^{+6} . Anions selected as model components included: CO_3^{-2} , Cl^{-} , F^{-} , NO_3^{-} , PO_4^{-3} , and SO_4^{-2} .

For all components except U(VI), CO_3^{-2} , and Ca^{+2} , the concentrations measured in the aqueous portions of the low pH batch test samples, which were the highest concentrations observed, were used for the models. These concentrations were equal to the amount of each component initially in the solutions plus the amount of each component that was dissolved from the soil at the low pH. As the model swept through the pH range, dissolved solids were reprecipitated. Modeling was performed in this manner because MINEQL+ does not allow for finite solids as did its predecessor, MINTEQA2, did.

The initial U(VI) concentration used for the geochemical model was determined through analysis of the U(VI)-spiked solutions prepared for the batch tests and/or the batch test quality assurance samples containing only spiked water. Carbonate concentrations were calculated using the weight percent of inorganic carbon measured in the soils. Table 5-2 shows the analytical results for the calibration and validation soil samples in regards to the soil carbon content.

It was assumed that all the inorganic carbon in the soil was in the form of calcium carbonate (CaCO_3) and that it was initially all dissolved in the batch test samples. The concentration was calculated according to the soil-to-liquid ratio in the samples; the concentration of Ca^{+2} was also calculated in this manner. The calculated Ca^{+2} concentrations were compared to the concentrations measured in the batch test samples, and the greater values were used. Specific concentrations for the geochemical model components are discussed in more detail in Sections 6.3.3 and 6.4.2.

Table 5-2. Soil carbon analytical results for geochemical model calibration and validation samples.

Sample	Weight Percent of Soil as			
	Total Carbon	Organic Carbon	Inorganic Carbon	Carbon as CaCO ₃
101B	0.13	0.04	0.09	0.77
104B	0.29	0.04	0.25	2.04
106B	0.54	0.07	0.47	3.90
112B	4.59	0.15	4.44	36.97
119B	0.05	0.02	0.03	0.21
121*	0.05	0.05	0.00	0.01
124*	0.05	0.03	0.02	0.20

*Data shown for samples 121 and 124 are from analysis of samples 120 and 124, respectively. These samples (120 and 124) were acquired directly above samples 121 and 124. Samples 121 and 124 were acquired specifically for the validation work and as a result were sealed until such time.

5.2.2.2 Aqueous Reactions

Aqueous reactions are those reactions in which two or more of the model components react to form a species that remains in solution. Given the number of model components used, the geochemical model took into account over 80 aqueous reactions. The aqueous reactions involving U(VI) and the respective equilibrium constants (K) are shown in Table 5-3. A complete list of the aqueous reactions used in the geochemical model is included in Appendix A.

5.2.2.3 Precipitation/Dissolution Reactions

Precipitation and dissolution of mineral species was also considered in the geochemical model efforts. The MINEQL+ geochemical model does not allow for finite amounts of solids to be initially present in the system; solids could only exist as fixed entities, which can dissolve, or dissolved species, which can precipitate. For each soil, with the exception of the caliche, no infinite solids were included in the geochemical model. For the caliche geochemical model, calcite (CaCO₃) was specified as an infinite solid.

Initially, modeling was completed without allowing any precipitation to take place. Saturation indexes were then examined to determine what solids were most likely to precipitate. The saturation index (SI) is defined by:

$$SI = \log \frac{Q}{K_{SP}} \quad (5-1)$$

where Q is the ion activity product of the solid, and K_{SP} ³ is the solubility product for the solid. Modeling was then adjusted to allow for precipitation of solids with an SI greater than zero and likely to be found in

³ The equilibrium constant, K, for a slightly soluble salt is termed the solubility product, K_{SP} .

the Hanford soils. Solids containing U(VI) that were allowed to precipitate are shown in Table 5-4. A complete list of the precipitation/dissolution reactions used in the geochemical model is included in Appendix B.

Table 5-3. Aqueous U(VI) reactions and equilibrium constants ($T=25\text{ }^{\circ}\text{C}$, $I=0$).

Species	Reaction	Log K
UO_2OH^+	$\text{UO}_2^{+2} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.2 ^{a, c, d, e, f}
$\text{UO}_2(\text{OH})_2$	$\text{UO}_2^{+2} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-11.5 ^f
$\text{UO}_2(\text{OH})_3^-$	$\text{UO}_2^{+2} + 3\text{H}_2\text{O} = \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	-19.4 ^e
$\text{UO}_2(\text{OH})_4^{-2}$	$\text{UO}_2^{+2} + 4\text{H}_2\text{O} = \text{UO}_2(\text{OH})_4^{-2} + 4\text{H}^+$	-33 ^{a, d, e, f}
$(\text{UO}_2)_2\text{OH}^{+3}$	$2\text{UO}_2^{+2} + \text{H}_2\text{O} = (\text{UO}_2)_2\text{OH}^{+3} + \text{H}^+$	-2.8 ^{d, e}
$(\text{UO}_2)_2(\text{OH})_2^{+2}$	$2\text{UO}_2^{+2} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{+2} + 2\text{H}^+$	-5.63 ^e
$(\text{UO}_2)_3(\text{OH})_4^{+2}$	$3\text{UO}_2^{+2} + 4\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_4^{+2} + 4\text{H}^+$	-11.9 ^{a, d, e, f}
$(\text{UO}_2)_3(\text{OH})_5^+$	$3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55 ^{c, e, f}
$(\text{UO}_2)_3(\text{OH})_7^-$	$3\text{UO}_2^{+2} + 7\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-31 ^{a, c, d, e, f}
$(\text{UO}_2)_4(\text{OH})_7^+$	$4\text{UO}_2^{+2} + 7\text{H}_2\text{O} = (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-21.9 ^{a, c, e, f}
$\text{UO}_2\text{CO}_3\text{ (aq)}$	$\text{UO}_2^{+2} + \text{CO}_3^{-2} = \text{UO}_2\text{CO}_3\text{ (aq)}$	9.67 ^{c, e}
$\text{UO}_2\text{ (CO}_3)_2^{-2}$	$\text{UO}_2^{+2} + 2\text{CO}_3^{-2} = \text{UO}_2\text{ (CO}_3)_2^{-2}$	17 ^{c, d, e}
$\text{UO}_2\text{ (CO}_3)_3^{-4}$	$\text{UO}_2^{+2} + 3\text{CO}_3^{-2} = \text{UO}_2\text{ (CO}_3)_3^{-4}$	21.63 ^{c, d, e}
UO_2F^+	$\text{UO}_2^{+2} + \text{F}^- = \text{UO}_2\text{F}^+$	5.09 ^{a, c, e, f}
$\text{UO}_2\text{F}_2\text{ (aq)}$	$\text{UO}_2^{+2} + 2\text{F}^- = \text{UO}_2\text{F}_2\text{ (aq)}$	8.62 ^{c, e, f}
UO_2F_3^-	$\text{UO}_2^{+2} + 3\text{F}^- = \text{UO}_2\text{F}_3^-$	10.9 ^{a, c, e, f}
$\text{UO}_2\text{F}_4^{-2}$	$\text{UO}_2^{+2} + 4\text{F}^- = \text{UO}_2\text{F}_4^{-2}$	11.7 ^{a, c, e, f}
$\text{UO}_2\text{NO}_3^{+1}$	$\text{UO}_2^{+2} + \text{NO}_3^- = \text{UO}_2\text{NO}_3^{+1}$	0.3 ^e
UO_2PO_4^-	$\text{UO}_2^{+2} + \text{PO}_4^{-3} = \text{UO}_2\text{PO}_4^-$	13.25 ^{b, e}
$\text{UO}_2\text{HPO}_4\text{ (aq)}$	$\text{UO}_2^{+2} + \text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{HPO}_4\text{ (aq)}$	19.655 ^{b, e}
$\text{UO}_2\text{H}_2\text{PO}_4^+$	$\text{UO}_2^{+2} + 2\text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{H}_2\text{PO}_4^+$	22.833 ^{b, e}
$\text{UO}_2\text{H}_3\text{PO}_4^{+2}$	$\text{UO}_2^{+2} + 3\text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{H}_3\text{PO}_4^{+2}$	22.47 ^{a, e}
$\text{UO}_2(\text{H}_2\text{PO}_4)_3\text{PO}_4^+$	$\text{UO}_2^{+2} + 5\text{H}^+ + 2\text{PO}_4^{-3} = \text{UO}_2(\text{H}_2\text{PO}_4)_3\text{PO}_4^+$	45.058 ^{d, e}
$\text{UO}_2(\text{H}_2\text{PO}_4)_3^-$	$\text{UO}_2^{+2} + 6\text{H}^+ + 3\text{PO}_4^{-3} = \text{UO}_2(\text{H}_2\text{PO}_4)_3^-$	66.245 ^b
$\text{UO}_2\text{H}_4(\text{PO}_4)_2\text{ (aq)}$	$\text{UO}_2^{+2} + 4\text{H}^+ + 2\text{PO}_4^{-3} = \text{UO}_2\text{H}_4(\text{PO}_4)_2\text{ (aq)}$	44.7 ^b
$\text{UO}_2\text{SO}_4\text{ (aq)}$	$\text{UO}_2^{+2} + \text{SO}_4^{-2} = \text{UO}_2\text{SO}_4\text{ (aq)}$	3.18 ^b
$\text{UO}_2\text{ (SO}_4)_2^{-2}$	$\text{UO}_2^{+2} + 2\text{SO}_4^{-2} = \text{UO}_2\text{ (SO}_4)_2^{-2}$	4.14 ^a
$\text{UO}_2\text{H}_3\text{SiO}_4^+$	$\text{UO}_2^{+2} + \text{Si(OH)}_4 = \text{UO}_2\text{H}_3\text{SiO}_4^+ + \text{H}^+$	-1.911 ^b

^a Allison et al., 1991

^b Schecher, 2001

^c Langmuir, 1997

^d Payne, 1999

^e Grenthe et al., 1992

^f Giammar, 2001

Table 5-4. Solid U(VI) reactions and equilibrium constants (T=25 °C, I=0).

Species	Reaction	Log K
Uranophane	$\text{Ca}^{+2} + 2\text{UO}_2^{+2} + 2\text{Si}(\text{OH})_4 = \text{Ca}(\text{UO}_2)_2[\text{SiO}_3(\text{OH})]_2 \cdot 5\text{H}_2\text{O} + 6\text{H}^+$	-17.49 ^b
$\text{UO}_2(\text{OH})_2$ (beta)	$\text{UO}_2^{+2} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-5.612 ^b
Rutherfordine	$\text{UO}_2^{+2} + \text{CO}_3^{-2} = \text{UO}_2\text{CO}_3$	14.5 ^b
Autunite	$\text{Ca}^{+2} + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$	44.7 ^a
H-Autunite	$2\text{H}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2$	48.42 ^a
K-Autunite	$2\text{K}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{K}_2(\text{UO}_2)_2(\text{PO}_4)_2$	48.244 ^b
Na-Autunite	$2\text{Na}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2$	47.6 ^a
$\text{UO}_2(\text{NO}_3)_2$	$\text{UO}_2^{+2} + 2\text{NO}_3^- = \text{UO}_2(\text{NO}_3)_2$	-12.148 ^b
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 2\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	-4.851 ^b
$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 3\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	-3.39 ^b
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 6\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	-2.046 ^b

^a Allison et al., 1991^b Schecher, 2001

5.2.2.4 Surface Complexation Data

The main parameters required for the diffuse-layer model include the type and concentration of sorbing sites and the thermodynamic equilibrium constants for reactions involving the sorbing sites and aqueous components. Historically, a great deal of surface complexation modeling has been based on results from well-controlled laboratory experiments. However, applying modeling results for these “pure” systems to more complex mineral assemblages may not be valid (Davis et al., 1998). MSE attempted to better characterize the sorbent through laboratory analytical measurements, optical microscopy, and a literature review.

As discussed earlier (Section 2.2), for the geochemical model efforts, iron was considered the primary sorbent for U(VI). Previous studies (Barnett et al., 2002, Payne, 1999, Waite et al., 1994, and Dzombak and Morel, 1990) have divided sorption sites on hydrous ferric oxide into two types: strong sites and weak sites. Weak sites, indicated by W in chemical formula, are the total reactive sites available for sorption of protons, cations, and anions; strong sites, indicated by S in chemical formula, are a smaller set of high-affinity cation binding sites (Dzombak and Morel, 1990). Both SOH and WOH were incorporated into MSE’s geochemical model efforts.

5.2.2.4.1 Sorbent Site Concentration

The concentration of sorbing sites in each soil sample was estimated from Equation 2-1 using the results from the CBD extract laboratory analytical work, optical microscopy, and a review of literature.

As discussed previously (Section 2.2), the CBD extract measured the total iron available for sorption. Optical microscopy was used to identify the specific form(s) of iron and relative percent abundance in the Hanford soils. MSE concluded that the primary forms of iron present in the soils included goethite ($\text{FeO} \cdot \text{OH}$) or limonite ($\text{FeOOH} \cdot n\text{H}_2\text{O}$), hematite (Fe_2O_3), and magnetite (Fe_3O_4) or ilmenite (FeTiO_3). The optical microscopy could not differentiate between goethite and limonite or magnetite and ilmenite. These two iron pairs are referred to in this document as goethite and magnetite, respectively. The mass of

each iron species (goethite, hematite, and magnetite) in a given mass of soil was calculated based on the CBD results and relative abundances estimated from the optical microscopy.

Identifying the specific form(s) of iron is key to better quantifying the concentration of surface sites. Nevertheless, this process is often overlooked and instead, it is assumed that all the iron exists as ferrihydrite (Barnett et al., 2002). Because of the significant differences in surface area and site density between ferrihydrite and other iron minerals, as will be shown, such an assumption can cause considerable error in site concentration calculations.

The number of sites contributed by each iron species depends on the surface area and site density of each iron species. As Table 5-5 shows, surface area and site density values vary among iron species.

Table 5-5. Surface area and site density values for common iron-bearing minerals.

Iron Mineral	Surface Area (m ² /g) ^a	Site Density (sites/nm ²) ^a
Goethite (FeO·OH)	45 – 169	2.6 – 18
Hematite (Fe ₂ O ₃)	1.8 – 3.1	5 – 22
Magnetite (Fe ₃ O ₄)	5 – 25 ^b	2.31 ^c
HFO (Fe ₂ O ₃ ·H ₂ O)	250 – 600	20

^a taken from Langmuir, 1997 unless otherwise noted
^b Walsh & Associates, Inc., 2003
^c Zavarin and Bruton, 1999

The final parameter needed for calculating the total sorption site concentration for a single iron species is the mass of the iron species in suspension. This parameter requires knowing the mass of soil that would be in contact with 1L of solution. Depending on the system being modeled (i.e., batch test sample, unsaturated soil, or saturated soil) this factor can also have a significant impact on the overall total site concentration.

MSE calculated the total concentration of sorbing sites as the sum of sorbing sites contributed by goethite, hematite, and magnetite. A strong-to-weak site ratio of 1 to 30 provided the best fit for the modeling and, therefore, was used for the geochemical model. This ratio falls within the range of strong and weak site densities reported in previous work (Dzombak & Morel, 1990).

5.2.2.4.2 Surface Complexation Reactions

Surface complexation equilibrium reactions used in the geochemical model 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. The surface complexation reactions used in the geochemical model are shown in Table 5-6.

As discussed in Section 2, the modeling approach used for this project combined the component additivity and generalized composite models. Total surface site concentrations were estimated based on the discrete iron phases (goethite, hematite, and magnetite) observed in the soil samples. However, surface complexation reactions (Table 5-6) were written for a single, general sorbent. Equilibrium constants for the surface complexation reactions were derived for each Hanford soil modeled. As discussed in Waite et al. (1994), the thermodynamic stability constants must be rederived when the

sorption site density changes. The iron-specific sorption site densities were kept constant throughout the geochemical model. However, the percent relative abundances of the iron species varied, causing the overall site density to change from soil to soil. The thermodynamic stability constants derived for the geochemical model are discussed further in Section 5.2.3.2 and Section 5.2.4.2.

Table 5-6. Surface complexation reactions used in the geochemical model.

Species	Reaction
SO ⁻	SOH = SO ⁻ + H ⁺
WO ⁻	WOH = WO ⁻ + H ⁺
SOH ₂ ⁺	SOH + H ⁺ = SOH ₂ ⁺
WOH ₂ ⁺	WOH + H ⁺ = WOH ₂ ⁺
SO ₂ -UO ₂	S(OH) ₂ + UO ₂ ⁺² = SO ₂ -UO ₂ + 2H ⁺
WO ₂ -UO ₂	W(OH) ₂ + UO ₂ ⁺² = WO ₂ -UO ₂ + 2H ⁺
SOH-Ca ⁺²	SOH + Ca ⁺² = SOH-Ca ⁺²
WO-Ca ⁺	WOH + Ca ⁺² = WO-Ca ⁺ + H ⁺
WO-Mg ⁺	WOH + Mg ⁺² = WO-Mg ⁺ + H ⁺
SO-Na	SOH + Na ⁺ = SO-Na + H ⁺
SOH – strong iron site	
WHO – weak iron site	

5.2.3 Geochemical Model Calibration

Calibration of the geochemical model was accomplished by adjusting the surface complexation parameters such that predicted data from the geochemical model agreed with measured, laboratory data. Laboratory data were obtained through a series of batch tests designed to assess U(VI) adsorption to the Hanford soils over a range of pH values.

An initial series of batch tests were completed in June 2002. These were followed by additional calibration batch tests that were finished in March 2003.

5.2.3.1 Additional Calibration Batch Tests

Review of the initial batch testing results (Section 4.3.3.2) indicated there were several issues that needed to be addressed before calibration of the geochemical model could be completed. These issues included those listed below.

- The final pH range reflected in the batch test samples was less (i.e., limited amount of data below pH of 5) than what was planned for. As a result, there was insufficient uranium adsorption data to calibrate the geochemical model.
- Due to the limited number of samples analyzed, several data outliers could not be explained. The lack of repeat samples and analysis did not allow for tracing possible errors in the batch testing or laboratory analysis.
- The amount of leachable uranium already present in the soil was not adequately quantified.

To address these issues, MSE performed additional batch tests in March 2003 (MSE, 2003a).

The additional batch tests were performed using the same five soils used in the previous batch tests. During the initial batch testing, MSE studied the effects that elevated CO₂ concentrations had on uranium adsorption. The additional batch tests were completed under ambient atmosphere conditions. Also, only one uranium concentration [approximately 2.5 milligrams per liter (mg/L)] was used for the additional calibration batch testing. The five soil samples used in the additional batch tests came from core samples collected during the installation of Well 299-W19-43. These are described in Table 5-7.

Table 5-7. Soil samples used for additional calibration batch tests.

Sample	Formation	Depth (ft)	Geologic Description
101B	Hanford Unit 1	21 – 22	Light brown gray (2.5Y 6/2) to grayish brown (2.5Y 5/2) sandy soil; Medium (1/4 to 1/2 mm) to coarse (1/2 to 1 mm) grained; Subrounded; 40% - 50% basalt, 2-3% magnetite; No visible reaction with HCl; Loose, dry soil
104B	Hanford Unit 2	111 – 112	Pale yellow (2.5Y 7/3) sandy soil; Very fine (1/8 to 1/4 mm) to fine (1/4 to 1/2 mm) grained; Rounded to subrounded; 5% basalt, <1-1% magnetite; Little to no reaction with HCl; Little to no moisture; Somewhat "cemented"
106B	Hanford Unit 2	171 – 172	Very pale brown (10YR 7/3) sandy to silty soil; Very fine (1/8 to 1/4 mm) grained; Subrounded; 1% - 2% basalt, Trace magnetite; Slight to moderate reaction with HCl; Little to no moisture; Loose to slightly cemented
112B	Plio-Pleistocene Caliche	195.2 – 196.2	Pale yellow (2.5Y 8/3 to 2.5Y 8/4) sandy silt; Silt (< 1/16 mm) to very fine (1/8 to 1/4 mm) grained; Subrounded; <1% - 1% basalt, Trace magnetite; Strong reaction with HCl; Highly cemented
119B	Upper Ringold	231 – 232	Light yellow brown (2.5Y 6/3) silty sand; Silt (< 1/16 mm) to very fine (1/8 to 1/4 mm) grained; Subrounded; <1% -1% basalt, Trace magnetite; No visible reaction with HCl; Moist

Columbia River water, collected near the Vernita Bridge, north of the Hanford Site, was used for the additional calibration batch testing. It is recognized that the chemical composition of the Columbia River water differs from that of the unsaturated and saturated groundwater and the discharged process waters; however, the Columbia River was a convenient, nonhazardous water source in the Hanford area. The geochemical model focuses on the uranium-soil interactions; consequently, changes in water chemistry can be accounted for. The Columbia River water was used in its raw form as well as spiked with uranyl-nitrate hexahydrate (UO₂(NO₃)₂·6H₂O) to simulate uranium-contaminated water. The spiked Columbia River water had a uranium concentration of approximately 2.5 mg/L (6.34×10⁻⁶ mol/L). Subolutions of the raw and spiked Columbia River water were prepared by adjusting the pH with either hydrochloric acid (HCl) for lower pH values or sodium hydroxide (NaOH) for higher pH values to achieve the desired (target) pH values (3 to 10). Quadruplicate batch test samples were prepared for each target pH. The percent of U(VI) that was removed from solution was calculated for each sample.

Results of the additional calibration batch tests are described in Summary of Additional Batch Testing Data for Calibration of the Geochemical Model (MSE, 2003b).

5.2.3.2 Geochemical Model of Calibration Results

Results from the additional calibration batch tests and analysis of the calibration soil samples were used to define the geochemical model surface complexation parameters. Sorbent site concentrations (see Section 5.2.2.4.1) were calculated using CBD extract and optical microscopy results. Optical microscopy and CBD extract results for the calibration soils are shown in Table 5-8.

Table 5-8. CBD and optical microscopy results for geochemical model of calibration soil samples.

Sample	CBD g Fe/kg Soil	% Relative Abundance of:		
		Goethite	Hematite	Magnetite
101B	1.66	16	10	74
104B	2.98	43	14	43
106B	3.76	25	50	25
112B	1.64	30	30	40
119B	3.85	84	11	5

Calculations also took into account the solid-to-aqueous ratio used in the batch tests [10 grams (g) of soil to 40 milliliters (mL) of solution] as well as the 1 to 30 strong-to-weak site ratio. The calculated sorbent site concentrations are shown in Table 5-9. Equilibrium constants for the surface complexation reactions estimated for each Hanford soil sample are shown in Table 5-10.

Table 5-9. Sorption site concentrations for geochemical model calibration.

Sample	Concentration (M) of:	
	SOH	WOH
101B	1.17×10^{-5}	3.51×10^{-4}
104B	5.32×10^{-5}	1.60×10^{-3}
106B	4.00×10^{-5}	1.20×10^{-3}
112B	2.08×10^{-5}	6.24×10^{-4}
119B	1.32×10^{-4}	3.97×10^{-3}

Initial concentrations of the aqueous components were determined through analysis of the batch test samples (see Section 5.2.2.1). These concentrations are shown in Table 5-11.

Using the model input described above and the information described in Sections 5.2.2.1 through 5.2.2.4, U(VI) adsorption was predicted for each Hanford soil sample and compared to the U(VI) adsorption measured in the batch tests. The following figures show the geochemical model results and how they compare to the measured adsorption. Two figures are presented for each soil sample. Figure 5-2 shows the major U(VI) species [aqueous, sorbed, and solid (i.e., precipitate)] the geochemical model predicted would form, and Figure 5-3 shows the percent of total U(VI) removed from solution, as predicted by the geochemical model and as measured in the laboratory. The laboratory results shown are averages of the multiple batch test samples for each target pH. The goodness-of-fit between the predicted and measured U(VI) adsorption data was evaluated quantitatively and qualitatively.

Table 5-10. Equilibrium constants for geochemical model calibration.

Surface Species	Log K Estimated for Sample:				
	101B	104B	106B	112B	119B
SO ⁻	-8.93	-8.93	-8.93	-8.93	-8.93
WO ⁻	-8.93	-8.93	-8.93	-8.93	-8.93
SOH ₂ ⁺	7.29	7.29	7.29	7.29	7.29
WOH ₂ ⁺	7.29	7.29	7.29	7.29	7.29
SO ₂ -UO ₂	7.65	5.4	7.45	7.5	6.5
WO ₂ -UO ₂	1.75	1.6	1.5	2.5	0.15
SOH-Ca ⁺²	10.3	12.7	11.7	13	13.5
WO-Ca ⁺	4.5	4.0	2.8	2.5	0.95
WO-Mg ⁺	-4.6	-4.6	-4.6	-4.6	-4.6
SO-Na	-0.55	-1.0	-0.25	-1.5	-0.35

Table 5-11. Aqueous component concentrations for geochemical model calibration.

Component	Concentration (M) for Sample:				
	101B	104B	106B	112B	119B
Al ⁺³	7.41×10^{-4}	8.71×10^{-4}	3.10×10^{-3}	3.15×10^{-5}	6.54×10^{-3}
Ca ⁺²	1.93×10^{-2}	5.11×10^{-2}	9.75×10^{-2}	9.25×10^{-1}	5.36×10^{-3}
Fe ⁺²	2.67×10^{-5}	1.44×10^{-4}	1.65×10^{-5}	1.25×10^{-5}	1.16×10^{-4}
K ⁺	7.55×10^{-4}	6.01×10^{-4}	7.23×10^{-4}	2.88×10^{-4}	5.37×10^{-4}
Mg ⁺²	4.24×10^{-3}	9.25×10^{-3}	1.45×10^{-2}	7.92×10^{-3}	6.16×10^{-3}
Mn ⁺³	2.00×10^{-4}	5.46×10^{-4}	4.00×10^{-4}	3.80×10^{-5}	3.91×10^{-4}
Na ⁺	1.28×10^{-3}	1.32×10^{-3}	3.19×10^{-3}	2.62×10^{-3}	2.26×10^{-3}
Si(OH) ₄	3.16×10^{-4}	2.44×10^{-3}	1.93×10^{-3}	1.14×10^{-3}	7.21×10^{-3}
UO ₂ ⁺²	5.44×10^{-6}	4.74×10^{-6}	5.44×10^{-6}	7.09×10^{-6}	6.85×10^{-6}
CO ₃ ⁻²	1.93×10^{-2}	5.11×10^{-2}	9.75×10^{-2}	9.42×10^{-1}	5.36×10^{-3}
F ⁻	5.26×10^{-6}	5.26×10^{-6}	5.26×10^{-6}	5.26×10^{-6}	5.26×10^{-6}
NO ₃ ⁻	1.13×10^{-5}	3.39×10^{-5}	7.42×10^{-5}	5.65×10^{-5}	8.23×10^{-5}
PO ₄ ⁻³	3.16×10^{-7}	3.16×10^{-7}	3.16×10^{-7}	3.16×10^{-7}	3.16×10^{-7}
SO ₄ ⁻²	2.08×10^{-4}	2.71×10^{-4}	2.19×10^{-4}	2.39×10^{-4}	3.64×10^{-4}

Figure 5-2. Major (a) aqueous, (b) sorption, and (c) solid U(VI) species predicted for sample 101B.

Figure 5-3. Predicted and measured U(VI) removed from solution for sample 101B.

The goodness-of-fit between the results was determined by calculating the root mean squared error (RMSE) according to Equation 4-3.

The major U(VI) species predicted by the geochemical model of soil sample 101B are shown in Figure 5-2. As Figure 5-2(a) shows, the major aqueous U(VI) species predicted to form include UO_2^{+2} as well as some uranyl-hydroxides ($\text{UO}_2(\text{OH})_2$ (aq) and $\text{UO}_2(\text{OH})_3^-$) and uranyl-carbonate complexes (UO_2CO_3 (aq), $\text{UO}_2(\text{CO}_3)_2^{-2}$, and $\text{UO}_2(\text{CO}_3)_3^{-4}$). Sorption occurs primarily on the strong sites with the lower pH adsorption edge occurring over a pH of about 2 to 3 [Figure 5-2(b)]. Here U(VI) sorption increases from 0% to around 80%. The upper pH edge slope is slightly more gradual with U(VI) sorption decreasing from around 80% to around 10% over a pH of about 6 to 7. From pH 7 to 8.5, U(VI) sorption decreases even more gradually. The geochemical model also predicts the formation of uranophane, $\text{Ca}(\text{UO}_2)_2[\text{SiO}_3(\text{OH})]_2 \cdot 5\text{H}_2\text{O}$ [Figure 5-2(c)], which precipitates over the pH range of about 8.5 to 10.5, accounting for almost 60% of the total U(VI) removed from solution at its maximum precipitation.

The total U(VI) removed from solution as predicted by the geochemical model and as measured in the laboratory are shown in Figure 5-3. The average relative standard deviation for all data from the 101B multiple batch test samples was 16%. The RMSE between the predicted and measured values for this soil was 0.08. The lower and upper pH edges predicted by the geochemical model match well with the measured data. The amount of U(VI) removed from solution at a pH of around 8 differs by about 15% between the predicted and measured results. There is also a difference of about 8% at pH 10 where the model predicted uranophane precipitation. Overall, the predicted and measured results show very good agreement.

Figure 5-4 shows the major U(VI) species predicted by the geochemical model for calibration with soil sample 104B. In the sample 104B geochemical model, the major aqueous U(VI) species predicted to form [Figure 5-4(a)] are UO_2^{+2} , $\text{UO}_2(\text{OH})_3^-$, UO_2CO_3 (aq), and $\text{UO}_2(\text{CO}_2)_2^{-2}$. Species such as $\text{UO}_2(\text{OH})_2$ (aq), UO_2CO_3 (aq), and $\text{UO}_2(\text{CO}_3)_3^{-4}$ are also present, but do not comprise a significant percentage of the total U(VI). U(VI) sorption [Figure 5-4(b)] occurs on both the strong and weak sites. Sorption to the strong sites increases dramatically (10% to 90%) over a pH range of 3 to 4 but decreases more gradually (90% to 20%) over a pH range of 5.5 to 7. U(VI) is also predicted to sorb, to a lesser extent, to weak sites. Sorption to the weak sites is distributed symmetrically over a pH range of 2 to 4. The maximum sorption to weak sites, just over 30%, occurs at a pH of about 3. Similar to the geochemical model for 101B, uranophane precipitates over the pH range of about 8.5 to 10.5 [Figure 5-4(c)].

Figure 5-5 shows the total U(VI) removed from solution as predicted by the geochemical model and as measured in the laboratory.

The average relative standard deviation for the multiple batch test samples for 104B was 9%. The RMSE between the predicted and measured values for this soil was 0.12. The lower pH adsorption edge and upper pH edge predicted by the geochemical model match well with the measured data. However, the upper pH edge, as predicted by the model, suggests U(VI) adsorption/precipitation stays above 15% -12% while the measured U(VI) adsorption/precipitation is around 8%. The predicted and measured results also show less agreement at the higher pH values (approximately 8 and 9). This is also the range where the model predicts precipitation of uranium becoming the dominant process of U(VI) removal from solution. Overall, the predicted and measured results show good agreement.

Figure 5-6 shows the major U(VI) species predicted by the geochemical model for calibration with soil sample 106B.

Results from the geochemical model of 106B are very similar to the results from the geochemical model of 104B. The major aqueous U(VI) species predicted to form [Figure 5-6(a)] are again UO_2^{+2} , $\text{UO}_2(\text{OH})_3^-$, UO_2CO_3 (aq), and $\text{UO}_2(\text{CO}_2)_2^{-2}$. Likewise, species such as $\text{UO}_2(\text{OH})_2$ (aq), UO_2CO_3 (aq), and $\text{UO}_2(\text{CO}_3)_3^{-4}$ are also present but still do not comprise a significant percent of the total U(VI). Sorption of U(VI) is predicted to occur on both the strong and weak sites [5-6(b)]. Sorption to the strong sites increases dramatically (5% to 95%) over a pH range of 2.5 to 4 but decreases more gradually (95% to 20%) over a pH range of 5 to 7. Sorption to the weak sites occurs over a pH range of 2 to 4 with the maximum sorption, about just over 38%, at a pH of about 3. The model also predicts uranophane precipitation [5-6(c)] over the pH range of about 8 to 10.5. At its maximum, the model predicts uranophane accounts for nearly 80% of the total U(VI) taken out of solution.

U(VI) removed from solution as predicted by the geochemical model and as measured in the laboratory is shown in Figure 5-7.

The average relative standard deviation for the multiple batch test sample measurements for sample 106B was 7%. The RMSE between the predicted and measured values was 0.10. The upper pH edge predicted by the geochemical model matches well with the measured data. Only one data point (pH approximately 3.5) from the measured results was near the low pH adsorption edge. Soil sample 106B had a higher inorganic carbon content (i.e., more calcite), most likely resulting in a higher buffering capacity. As a result, it was more difficult to lower the pH in the batch test samples. Nonetheless, there is excellent agreement between the modeled and measured results at the low pH point. The only place having relatively poor agreement between the predicted and measured results was at the upper pH. Like the previous models, the geochemical model for soil 106B predicted uranophane precipitation over the pH range 8 to 10.5. While the model predicted around 76% of the total U(VI) removed from solution, the measured value was only about 62%. Overall, the predicted and measured results show very good agreement.

Figure 5-4. Major (a) aqueous, (b) sorption, and (c) solid U(VI) species predicted for sample 104B.

Figure 5-5. Predicted and measured U(VI) removed from solution for sample 104B.

Figure 5-6. Major (a) aqueous, (b) sorption, and (c) solid U(VI) species predicted for sample 106B.

Figure 5-7. Predicted and measured U(VI) removed from solution for sample 106B.

Geochemical model of sample 112B was performed in a slightly different way than the other soils samples. Sample 112B was acquired from the caliche layer located at the base of the Plio-Pleistocene formation, which is described as a sandy silt highly cemented by calcium-carbonate. Because of the excessive amount of calcium-carbonate in the soil (estimated to be about 37% by weight as shown in Table 5-2), calcite was included in the model as a fixed entity. The calcium-carbonate also gave the soil a very high buffering capacity, preventing the batch test samples from achieving a pH less than 6.

Figure 5-8 shows the major U(VI) species predicted by the geochemical model for calibration with soil sample 112B. As Figure 5-8(a) shows, the dominant aqueous U(VI) species include UO_2^{+2} , $\text{UO}_2(\text{OH})_3^-$, UO_2CO_3 (aq), and $\text{UO}_2(\text{CO}_2)_2^{-2}$. $\text{UO}_2(\text{OH})_2$ (aq) and $\text{UO}_2(\text{CO}_3)_3^{-4}$ are also present. Sorption [Figure 5-8(b)] is predominantly on the strong sites but is significantly shifted along the pH axis. The lower pH adsorption edge occurs over a pH of about 5 to 6.5. Here U(VI) sorption increases from 0% to around 70%. The percent of U(VI) adsorbed does not exceed about 72%. The upper pH edge slope decreases from around 70% to around 0% over a pH of about 8 to 9. The geochemical model predicts uranophane precipitation [Figure 5-10(c)] over the pH range of about 8.2 to 10.5, accounting for almost 75% of the total U(VI) removed from solution at its maximum precipitation.

The total U(VI) removed from solution as predicted by the geochemical model and as measured in the laboratory is shown in Figure 5-9.

The average relative standard deviation for all measured data from the 112B batch test samples was 5%. The RMSE between the predicted and measured values was 0.13. The lower pH adsorption edge predicted by the geochemical model matches well with the measured data. At higher pHs, the predicted and measured results show less agreement. Unlike the previous models where the predicted results were often greater than the measured results for uranophane precipitation, the measured results from sample 112B are about 15% higher than the adsorption/precipitation. Overall, the predicted and measured results show good agreement.

Finally, Figure 5-10 shows the major U(VI) species predicted by the geochemical model for calibration with soil sample 119B. Major aqueous U(VI) species predicted [Figure 5-10(a)] include UO_2^{+2} , $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_2)_2^{-2}$, and $\text{UO}_2(\text{CO}_3)_3^{-4}$. UO_2CO_3 (aq) and $\text{UO}_2(\text{OH})_2$ (aq) are also present. Unlike soil sample 112B, the amount of calcium-carbonate in soil sample 119B is slight (estimated to be about 0.2% by weight as shown in Table 5-2). Not surprisingly, the uranyl-carbonate species are not as prominent. U(VI) sorption [Figure 5-10(b)] over the pH range modeled occurs primarily on the weak sites, while is in contrast to the previous geochemical model results. The lower pH adsorption edge occurs over a pH of about 2 to 3.5, increasing from 0% to around 100%. The upper pH edge slope decreases sharply from around 100% to around 50% over a pH of about 6 to 7. Sorption decreases more gradual (about 10%) from pH 7 to 8.5 before finally returning to 0% at a pH of about 9. The geochemical model predicts uranophane precipitation [Figure 5-10(c)] over the pH range of about 8.8 to 10.5. Only about 30% of the total U(VI) removed from solution is attributed to the uranophane over this pH range. The total U(VI) removed from solution as predicted by the geochemical model and as measured in the laboratory are shown in Figure 5-11. The average relative standard deviation for all measured data from the 119B batch test samples was 3%. The RMSE between the predicted and measured values was 0.18. The lower pH adsorption edge predicted by the geochemical model matches well with the measured data. The upper edge shows less agreement with the measured data but, in general, the shape of the predicted results match the measured results. The highest pH observed in the measured data was around 8.8. Consequently, the accuracy of the modeling above pH 9 cannot be evaluated. Overall, the predicted and measured results show good agreement.

(a)

(b)

(c)

Figure 5-8. Major (a) aqueous, (b) sorption, and (c) solid U(VI) species predicted for sample 112B.

Figure 5-9. Predicted and measured U(VI) removed from solution for sample.

(a)

(b)

(c)

Figure 5-10. Major (a) aqueous, (b) sorption, and (c) solid U(VI) species predicted for sample 119B.

Figure 5-11. Predicted and measured U(VI) removed from solution for sample 119B.

5.2.4 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.

5.2.4.1 Validation Batch Tests

The batch tests for validating the geochemical model were completed in July 2003. A detailed description of these batch tests can be found in MSE, 2003c.

The validation batch tests were performed using soil samples 121 and 124 acquired during the drilling of borehole 299-W19-43. These samples were acquired specifically for validating the geochemical model and were sealed until validation work began. To ensure enough material was available for both the validations batch tests and soil/groundwater analysis, MSE also acquired samples 120 and 123, which were taken immediately above samples 121 and 124, respectively. The soil samples used in the validation batch tests are described in Table 5-12.

Table 5-12. Soil samples used for validation batch tests.

Sample	Formation	Depth (ft)	Geologic Description
120 and 121	Upper Ringold	245 – 247 and 247 – 249	Light yellow brown (2.5Y 6/3) sandy silt; Very fine (1/16 to 1/8 mm) to silt (<1/16 mm) grained; Rounded to subrounded; ~5% basalt, quartz dominant, ~1% magnetite; reddish-orange staining on some grains; No visible reaction with HCl; Slightly compacted; Well sorted; Slight to no moisture; Few cobbles present with amount increasing with depth
123 and 124	Hanford Unit 2	270 – 272 and 272.5 – 274.5	Gravels and cobbles with sandy matrix Matrix: Olive brown (2.5Y 4/3 to 2.5 Y 4/4) sand; Fine (1/8 to 1/4 mm) to very fine (1/4 to 1/2 mm) grained; Subrounded; ~5% basalt, quartz dominant, little magnetite; No reaction with HCl; Wet

Analytical work (see FY02 Status Report, MSE, 2002a), was performed on samples 120 and 123 to characterize the soils represented by the sample pairs.

Uncontaminated groundwater used in the validation batch tests was acquired from well 699-55-89, which is approximately 2 miles upgradient of the study area. The water from well 699-55-89 had a higher dissolved solids content than the groundwater currently in well 299-W19-43. The lower total dissolved solids in well 299-W19-43 is attributed to dilution occurring while the initial pump-and-treat operation was injecting water back into the ground. Since the injection has stopped, it is believed that the chemical composition groundwater in the study area and well 299-W19-43 will equilibrate back to a composition resembling that found in well 699-55-89.

The well 699-55-89 water was used in its raw form as well as 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 uranium concentration used for validating the geochemical model was approximately 1.4 mg/L (5×10^{-6} M), which was similar to the concentration used in the additional calibration batch tests (2.5 mg/L or 6.34×10^{-6} mol/L). Subsamples 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).

5.2.4.2 Geochemical Model of the Validation Batch Tests

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 (see Section 5.2.2.4.1) were calculated using CBD extract and optical microscopy results. Optical microscopy and CBD extract results for the validation soils are shown in Table 5-13.

Calculations also took into account the solid-to-aqueous ratio used in the batch tests (10 g to 40 mL) as well as the strong-to-weak site ratio of 1:30. The calculated sorbent site concentrations are shown in Table 5-14, and the equilibrium constants used for the validation geochemical model are shown in Table 5-15.

Table 5-13. CBD and optical microscopy results for geochemical model of validation soil samples.

Sample	CBD g Fe/kg Soil ¹	% Relative Abundance of: ²		
		Goethite	Hematite	Magnetite
120 and 121	3.77	23	3	74
123 and 124	3.84	27	4	68

¹ Results from analysis of samples 121 and 124
² Results from analysis of samples 120 and 123

Table 5-14. Sorption site concentrations for geochemical model validation.

Sample	Concentration (M) of:	
	SOH	WOH
121	1.17×10^{-5}	3.51×10^{-4}
124	5.32×10^{-5}	1.60×10^{-3}

Table 5-15. Derived equilibrium constants for geochemical model validation.

Surface Species	Log K Derived for Sample:	
	121	124
SO ⁻	-8.93	-8.93
WO ⁻	-8.93	-8.93
SOH ₂ ⁺	7.29	7.29
WOH ₂ ⁺	7.29	7.29
SO ₂ -UO ₂	6.5	6.5
WO ₂ -UO ₂	1.9	1.65
SOH-Ca ⁺²	12.85	11.9
WO-Ca ⁺	3.75	3.27
WO-Mg ⁺	-4.6	-4.60
SO-Na	-0.08	-0.7

Initial concentrations of the aqueous components were determined through analysis of the batch test samples (see Section 5.2.2.1). These concentrations are shown Table 5-16.

Table 5-16. Aqueous component concentrations for geochemical model validation.

Component	Concentration (M) for Sample:	
	121	124
Al ⁺³	8.65×10^{-4}	2.84×10^{-3}
Ca ⁺²	6.29×10^{-3}	9.93×10^{-3}
Fe ⁺²	9.17×10^{-5}	4.00×10^{-6}
K ⁺	4.09×10^{-4}	6.56×10^{-4}
Mg ⁺²	2.07×10^{-3}	3.84×10^{-3}
Mn ⁺³	2.55×10^{-4}	3.58×10^{-4}
Na ⁺	9.86×10^{-4}	9.28×10^{-4}
Si(OH) ₄	3.88×10^{-3}	6.03×10^{-3}
UO ₂ ⁺²	4.81×10^{-6}	4.81×10^{-6}
CO ₃ ⁻²	2.69×10^{-4}	4.98×10^{-3}
F ⁻	3.32×10^{-4}	6.84×10^{-4}
NO ₃ ⁻	1.43×10^{-4}	2.18×10^{-4}
PO ₄ ⁻³	8.39×10^{-5}	3.75×10^{-4}
SO ₄ ⁻²	1.98×10^{-4}	2.39×10^{-4}

Using the model input described above and the information described in Sections 0 through 0, U(VI) adsorption was predicted for samples 121 and 124. The predicted results were then compared to the U(VI) adsorption measured in the batch tests. The following figures (5-12 through 5-15) show the validation geochemical model results and how they compare to the measured adsorption; two figures are presented for each soil sample. The first figure shows the major U(VI) species (aqueous, sorption, and solid) that would form per the geochemical model predictions, and the second figure shows the percent of total U(VI) removed from solution as predicted by the geochemical model and as measured in the laboratory. The goodness-of-fit between the predicted and measured U(VI) adsorption data was evaluated both quantitatively and qualitatively.

The goodness-of-fit between the results was determined by calculating the RMSE according to Equation 4-3.

The major U(VI) species predicted by the geochemical model of soil sample 121 are shown in Figure 5-12 for comparison with the calibration models, and to provide a complete geochemical model of the uranium partitioning.

(a)

(b)

(c)

Figure 5-12. Major (a) aqueous, (b) sorption, and (c) solid U(VI) species predicted for sample 121.

The primary U(VI) species formed, as predicted by the model, for soil 121 are shown in Figure 5-12(a), and include UO_2^{+2} and the uranyl-hydroxides and uranyl-carbonates. The calibration models also predicted these species. Of the uranyl-hydroxides, $\text{UO}_2(\text{OH})_3^-$ appears more likely to form. $\text{UO}_2(\text{CO}_3)_2^{-2}$ is the more dominant uranyl-carbonate followed by $\text{UO}_2(\text{CO}_3)_3^{-4}$ and finally $\text{UO}_2\text{CO}_3(\text{aq})$. Overall, U(VI) sorption [Figure 5-12(b)] to the strong sites is only slightly more prevalent. Strong and weak site adsorption are shifted apart from one another over the pH range modeled. The weak site adsorption is distributed over a pH range of about 2 to 5.5 (maximum of about 85% at pH 3.5) while the strong site adsorption is distributed over a pH range of 3.5 to 8 (maximum of about 95% at pH 5.5). Solid species predicted to form [Figure 5-12(c)] include autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$) and uranophane. Autunite is predicted to precipitate over a pH range of about 5.5 to 8 (maximum of about 90% at pH 7). Autunite formation could be attributed to the higher phosphate concentration measured in the validation-batch-test samples. Uranophane is predicted to start precipitating at a pH of about 8. Almost 70% of the total U(VI) removed from solution over the pH range of 8 to 11 is a result of uranophane precipitation.

The total U(VI) removed from solution as predicted by the geochemical model and as measured in the laboratory is shown in Figure 5-13.

Figure 5-13. Predicted and measured U(VI) removed from solution for sample 121.

The average relative standard deviation for the measurements from the multiple batch test samples for soil sample 121 was 3%. The RMSE between the predicted and measured values was 0.28. The lower pH adsorption edge predicted by the geochemical model matches well with the measured data. The upper edge shows less agreement, leading to the higher RMSE value. The predicted upper pH edge appears to be shifted about a half of a pH unit. The measured adsorption at the highest pH (about pH 10.8) also shows less agreement with the model. Here the predicted adsorption is about 10% less than the measured adsorption. Aside from these disparities, the predicted and measured results show very good agreement.

The major U(VI) species predicted by the geochemical model of soil sample 124 are shown in Figure 5-14. Major aqueous U(VI) species predicted [Figure 5-14(a)] include UO_2^{+2} and the uranyl-hydroxides and uranyl-carbonates seen in previous models. In addition to UO_2^{+2} , other uranium species (i.e., $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_2)_2^{-2}$, and $\text{UO}_2(\text{CO}_3)_3^{-4}$) are the more prevalent species. UO_2CO_3 (aq) and $\text{UO}_2(\text{OH})_2$ (aq) are predicted to be in solution but at a lower percent of the total U(VI). Total U(VI) sorption [Figure 5-14(b)] resembles the sorption seen in calibration sample 119B. However, in sample 124, U(VI) sorption occurs primarily on the strong sites. Sorption on the strong sites is predicted to occur over a pH range of about 2 to 9, with 100% of the total U(VI) predicted to adsorb over the pH range of about 4.5 to 6.5. Weak site adsorption occurs over a pH of about 2.5 to 4.5. Maximum U(VI) adsorption to the weak surface sites is almost 60% at a pH of about 3. Unlike sample 121 where both autunite and uranophane were predicted to precipitate, in sample 124 uranophane is the only solid species predicted to form [Figure 5-14(c)]. Around 60% of the total U(VI) removed from solution over the pH range of 8.2 to 11 results from uranophane precipitation.

The total U(VI) removed from solution as predicted by the geochemical model and as measured in the laboratory are shown in Figure 5-15. The average relative standard deviation for the data from the multiple batch test samples for soil 124 was 15%. The RMSE between the predicted and measured values was 0.06. The lower pH adsorption edge predicted by the geochemical model matches well with the measured data. The upper edge also shows good agreement. The measured results near pH 7.4 agree least with the predicted results. The model predicts about 45% of the total U(VI) removed from solution while the measured results indicate only 38% was removed. Overall, the predicted and measured results show very good agreement.

(a)

(b)

(c)

Figure 5-14. Major (a) aqueous, (b) sorption, and (c) solid U(VI) species predicted for sample 124.

Figure 5-15. Predicted and measured U(VI) removed from solution for sample 124 geochemical model validation.

5.2.5 Geochemical Model Discussion/Conclusions

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, predicted and measured results from the calibration samples showed the same general shape and adsorption values. 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 (e.g., Zavarin and Bruton, 1999) that investigated how the type and concentration of iron species and the carbonate concentration control U(VI) adsorption.

6. FISCAL YEAR 2004 ACTIVITIES

FY04 activities included performing chloride (Cl^-) and sodium (Na^+) sensitivity analyses on the geochemical model; U-236 isotopic analyses performed on soil samples from the 200 West Area; and updating the current site conceptual model. The efforts associated with these activities are detailed in this report.

6.1 Cl^- AND Na^+ SENSITIVITY ANALYSES

At a meeting with Hanford Site representatives in November 2003, MSE was asked to consider the sensitivity of the geochemical model to the concentrations of Cl^- and Na^+ in solution. These components were identified because of their presence in the acid (HCl) and base (NaOH) used to adjust the pH of model calibration and validation batch test samples. The sensitivity analysis was completed using the calibration and validation geochemical models developed in FY03 (MSE, 2003d) for the soils associated with the 216-U1/U2 Cribs in the 200 West Area of the Hanford Site. These models were developed under the MINEQL+[®] v. 4.5 software package (Schecher and McAvoy, 2001).

Sensitivity models were run by varying the initial Cl^- and Na^+ aqueous concentration. Initial Cl^- and Na^+ aqueous concentrations covered the range of concentrations measured in the calibration and validation batch test samples. Table 6-1 shows the Cl^- and Na^+ concentrations measured in the batch test samples, used in the geochemical modeling, and used in the sensitivity analysis.

Table 6-1. Summary of Cl^- and Na^+ concentrations for sensitivity modeling.

	[Cl^-]	[Na^+]
Batch Test Samples	Min – 1.10×10^{-4} M Max – 4.40×10^{-2} M	Min – 6.05×10^{-5} M Max – 7.53×10^{-3} M
Calibration and Validation Modeling	Not Used*	Sample – Concentration 101B – 1.28×10^{-3} M 104B – 1.32×10^{-3} M 106B – 3.19×10^{-3} M 112B – 2.62×10^{-3} M 119B – 2.26×10^{-3} M 121 – 9.86×10^{-4} M 124 – 9.28×10^{-4} M
Sensitivity Modeling	1×10^{-4} M, 1×10^{-3} M, 1×10^{-2} M, and 1×10^{-1} M,	5×10^{-5} M, 1×10^{-4} M, 5×10^{-4} M, 1×10^{-3} M, and 5×10^{-3} M
* Cl^- was not included as a component in the calibration and validation geochemical models.		

As Figure 6-1 shows, the concentrations of Cl^- and Na^+ varied more significantly over specific pH ranges.

Figure 6-1. *Cl and Na concentrations measured in batch test samples vs. pH.*

The pH ranges corresponded to the batch test samples that were altered by either HCl or NaOH. Cl⁻ concentrations varied over a pH range of about 1 to 8 and were fairly constant at pHs above 8. Na concentrations varied over a pH range of about 9 to 11 and were fairly constant at pHs below 9. Batch test samples that had no addition of HCl or NaOH typically had a pH between 8 and 9. As a result of this data, MSE modeled Cl⁻ sensitivity of the pH range of 1 to 8 and Na sensitivity over the pH range of 8 to 11.

Because Cl⁻ was not a component of the previous modeling, 3 additional aqueous reactions were added to the models. These reactions are shown in Table 6-2.

Table 6-2. *Aqueous Cl⁻ reactions and equilibrium constants (T=25 °C, I=0).*

Species	Reaction	Log K
FeCl ⁺	Fe ⁺² + Cl ⁻ = FeCl ⁺	-0.20 ^a
UO ₂ Cl ⁺	UO ₂ ⁺² + Cl ⁻ = UO ₂ Cl ⁺	0.21 ^a
UO ₂ Cl ₂	UO ₂ ⁺² + 2Cl ⁻ = UO ₂ Cl ₂	-1.10 ^a

^a Schecher, 2001

6.1.1 Cl⁻ Sensitivity Modeling Results

Cl⁻ sensitivity models were run for each of the geochemical models developed for the 7 Hanford soils comprising the calibration and validation efforts. Results of the Cl⁻ sensitivity are shown in Figure 6-2 as % of total U(VI) removed from solution versus pH.

The geochemical models show no significant change over the pH range of 1 to 8 as the Cl⁻ concentration is varied. This indicates that the geochemical models for these soils are not sensitive to the aqueous Cl⁻ concentration.

Figure 6-2. Cl sensitivity analysis results.

6.1.2 Na⁺ Sensitivity Modeling Results

Na⁺ sensitivity analyses were also run on the calibration and validation geochemical models. Results are shown in Figure 6-3 as % of total U(VI) removed from solution versus pH.

Results of the Na⁺ sensitivity analysis show no significant changes in the models in the pH range of about 9 to 11. Above pH 9, precipitation begins dominating U(VI) removal from solution, making sorption site competition less important. As a result, the model is less sensitive to Na⁺. Below a pH of 9 however, the model appears to be sensitive to the initial concentration of Na in solution. As the Na⁺ concentration increases, the percentage of U(VI) removed from solution decreases. The differences in models at this pH range are likely a result of competition between Na⁺ and U(VI) for sorption sites. The sensitivity model and original geochemical model with similar Na concentrations (i.e., 10⁻³ M) show only slight differences.

Figure 6-3. Na sensitivity analysis results.

6.2 U-236 ISOTOPE STUDY

As discussed in Section 5.1, in FY03 MSE completed a uranium isotope analysis on the caliche samples from the Hanford site and surrounding area. The spectroscopy results showed that the uranium in most of the samples appears to be naturally occurring. However, on the suggestion of Jeff Serne of Pacific Northwest National Laboratory, MSE submitted a set of soil samples to Don DePaulo of the University of California at Berkeley for a more sensitive mass spectroscopy analysis.

The mass spectroscopy method performed at Berkeley analyzed the soil samples for U-236. The U-236 isotope is not naturally present. As a result, if detected in the soil samples, the presence of U-236 would be a direct indication of Hanford waste in the soil.

The mass spectroscopy analyses had not been completed at the time this report was written. When available, results will be provided.

6.3 UPDATING THE CURRENT SITE CONCEPTUAL MODEL

The major task completed in FY04 was the updating of the site conceptual model of uranium mobility in the unsaturated and saturated soils associated with the 216-U1/U2 Cribs to reflect the geochemical

modeling results obtained in FY03. Updating the current conceptual model meant 1) evaluating the validity of the current conceptual model; 2) determining the potential for uranium in the vadose zone under the U1/U2 Cribs being a continuing source for the groundwater uranium plume in the area; and 3) assessing the current remedial action (i.e., capping of the U1/U2 Cribs) proposed for the site.

To accomplish this MSE performed a number of uranium transport simulations and compared the predicted and observed concentrations of uranium in the groundwater. MSE modeled the chemical processes (i.e., aqueous speciation, surface complexation, and precipitation) between waste, specifically uranium, and the native pore waters and sediments associated with the U1/U2 Cribs. The one-dimensional (1D) advection and mixing functions of PHREEQCI were used along with the chemical/geochemical parameters of the waste, sediments, and ground water associated with the U1/U2 Cribs. The modeling completed by MSE included some transport elements and considered more complicated geochemical processes (i.e., surface complexation). However, these modeling efforts should not be compared to modeling performed numerical solute transport models that work within a modeling environment that is well discretized with respect to space and time.

6.3.1 Modeling Software

Most of the geochemical modeling associated with updating the conceptual model was completed using the computer program PHREEQCI (Parkhurst, 1999). PHREEQCI, or PHREEQC-Interactive, is a public domain geochemical modeling program developed and supported by the U.S. Geological Survey (USGS). The acronym PHREEQCI stands for pH, redox equilibrium, and C stands for C programming language. PHREEQCI contains the modeling code of PHREEQC V2 and also provides a Windows-based, graphical user interface. PHREEQCI has all the modeling capabilities of PHREEQC including speciation, batch-reaction, one-dimensional reactive-transport, advection, and inverse modeling.

MSE used PHREEQCI v2.8.0.0, dated April 15, 2003, for the modeling efforts. This version was obtained from the USGS web site: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqci.

6.3.2 Modeling Approach

The PHREEQCI geochemical modeling efforts focused on the processes (aqueous speciation, surface complexation, and precipitation) that may have controlled the uranium mobility beneath the U1/U2 Cribs. The key modeling elements included simulating 1D advective transport of the U1/U2 Crib wastes to the aquifer, mixing of contaminated water from the unsaturated zone with the aquifer water, and advective transport of atmospheric water through the contaminated sediments. Several scenarios were considered for the potential pathways of the U1/U2 waste to the aquifer. The scenarios were also modeled using a range of parameter values (e.g., unsaturated soil column volume, water saturation ratio, waste pore volumes, mixing ratios, etc.). Each model predicted uranium concentrations at the water table interface and in the aquifer that could be compared to measured, historical concentrations or used to predict future concentrations.

6.3.3 Data Sources

The primary input data for the PHREEQCI modeling included the concentrations of the species in the various aqueous solutions, concentrations of sorption sites in the sediments, thermodynamic constants for the aqueous, surface complexation, and solid species, advection parameters, and mixing parameters.

Aqueous solutions used in the modeling scenarios included: the waste disposed to the U1/U2 Cribs; the initial water in the sediments; the water initially making up the aquifer; and atmospheric water. The U1/U2 Crib waste chemistry was taken from the waste inventory report prepared by MSE (MSE, 2002c).

The initial chemistry of the aquifer water was assumed to be similar to that measured in Hanford well 699-55-89, which is just west of the 200 West Area, upgradient of the project site. Atmospheric water chemistry was taken from data reported by the Palouse Conservation Farm National Atmospheric Deposition Program observation station. Chemical compositions input to the models for these three solutions are shown in Table 6-3.

Table 6-3. Chemistry of U1/U2 waste, well 699-55-89 water, and atmospheric water used in PHREEQCI modeling.

Master Species	Concentration (mol/kg)		
	U1/U2 Crib Waste	Well 699-55-89 Water	Atmospheric Water
Al ⁺³	4.75×10^{-2}	5.56×10^{-6}	
Ca ⁺²	2.50×10^{-3}	8.16×10^{-4}	1.15×10^{-5}
Fe ⁺³	2.86×10^{-3}	1.93×10^{-6}	
K ⁺	3.32×10^{-3}	1.09×10^{-4}	4.19×10^{-6}
Mg ⁺²	2.06×10^{-3}	5.18×10^{-4}	3.17×10^{-6}
Mn ⁺²		9.10×10^{-8}	
NH ₄ ⁺			6.40×10^{-5}
N ⁺⁵	6.21×10^{-1}	7.08×10^{-5}	1.98×10^{-4}
Na ⁺	6.96×10^{-1}	4.65×10^{-4}	1.38×10^{-5}
UO ₂ ⁺²	3.24×10^{-4}	3.20×10^{-8}	
CO ₃ ⁻²	3.69×10^{-3}		
Cl ⁻	2.26×10^{-2}		1.23×10^{-5}
F ⁻	4.21×10^{-4}	1.58×10^{-5}	
PO ₄ ⁻³	2.40×10^{-2}	3.79×10^{-7}	
SO ₄ ⁻²	3.44×10^{-2}	4.38×10^{-5}	2.37×10^{-5}
H ₃ SiO ₄	1.05×10^{-3}	7.21×10^{-4}	
Alkalinity as HCO ₃		1.98×10^{-3}	
pH	6.00	7.95	5.35
pe	6.76	6.30	4.00
Density (kg/L)	1.025	1.000	1.000

Chemistries of the initial water in the sediments were obtained from the laboratory analysis of the sediments. These analyses were completed by Pacific Northwest National Laboratory in October 2001 and were included in the FY02 status report (MSE, 2002a).

Concentrations of sorbing surface sites used for the PHREEQCI modeling were estimated in the same manner as for the geochemical modeling efforts completed in FY03 (MSE, 2003d). Sorption site concentrations are based on the amount of sorbent (i.e., goethite, hematite, and magnetite) in contact with one liter of solution (i.e., groundwater). For the PHREEQCI modeling, sorption site concentrations were dependent on the water saturation conditions simulated for the vadose zone and in the aquifer. Figure 6-4 illustrates how the saturation affects the concentration of sorption sites (Γ_{SOH}).

Figure 6-4. Impact of moisture content on the concentration of sorbing surface sites.

As Figure 6-4 shows, an increase in the sediment saturation decreases the sorption site concentration. The PHREEQCI modeling efforts considered a range of saturation values, correcting the sorption site concentrations as needed.

Thermodynamic constants used for the PHREEQCI modeling were taken from the modeling work performed in FY03 (MSE, 2003d). These data included thermodynamic constants for aqueous, surface complexation, and solid species. Thermodynamic constants for the U(VI) aqueous, surface complexation, and solid species are shown in Table 6-4, Table 6-5, and Table 6-6, respectively.

Most advection parameters and mixing parameters were estimated according to additional historical data and/or analytical data. Flow rate for the PHREEQCI geochemical modeling of uranium contaminated waste and atmospheric water advection downward through the vadose zone was simulated using the number of pore volumes. The number of waste pore volumes was a function of the volume of waste disposed to U1/U2 Cribs, the volume of soil the waste moved through, and the water saturation ratio. The volume of waste disposed to U1/U2 Cribs (between 1956 and 1963) was estimated to be $46,200 \text{ m}^3$ (MSE, 2002). Advection and mixing parameters are discussed in greater detail in Section 0.

Table 6-4. Aqueous U(VI) reactions and equilibrium constants (T=25 °C, I=0).

Species	Reaction	log K
UO_2OH^+	$\text{UO}_2^{+2} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.2 ^{a, c, d, e, f}
$\text{UO}_2(\text{OH})_2$	$\text{UO}_2^{+2} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-11.5 ^f
$\text{UO}_2(\text{OH})_3^-$	$\text{UO}_2^{+2} + 3\text{H}_2\text{O} = \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	-19.4 ^e
$\text{UO}_2(\text{OH})_4^{-2}$	$\text{UO}_2^{+2} + 4\text{H}_2\text{O} = \text{UO}_2(\text{OH})_4^{-2} + 4\text{H}^+$	-33 ^{a, d, e, f}
$(\text{UO}_2)_2\text{OH}^{+3}$	$2\text{UO}_2^{+2} + \text{H}_2\text{O} = (\text{UO}_2)_2\text{OH}^{+3} + \text{H}^+$	-2.8 ^{d, e}
$(\text{UO}_2)_2(\text{OH})_2^{+2}$	$2\text{UO}_2^{+2} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{+2} + 2\text{H}^+$	-5.63 ^e
$(\text{UO}_2)_3(\text{OH})_4^{+2}$	$3\text{UO}_2^{+2} + 4\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_4^{+2} + 4\text{H}^+$	-11.9 ^{a, d, e, f}
$(\text{UO}_2)_3(\text{OH})_5^+$	$3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55 ^{c, e, f}
$(\text{UO}_2)_3(\text{OH})_7^-$	$3\text{UO}_2^{+2} + 7\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-31 ^{a, c, d, e, f}
$(\text{UO}_2)_4(\text{OH})_7^+$	$4\text{UO}_2^{+2} + 7\text{H}_2\text{O} = (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-21.9 ^{a, c, e, f}
$\text{UO}_2\text{CO}_3(\text{aq})$	$\text{UO}_2^{+2} + \text{CO}_3^{-2} = \text{UO}_2\text{CO}_3(\text{aq})$	9.67 ^{c, e}
$\text{UO}_2(\text{CO}_3)_2^{-2}$	$\text{UO}_2^{+2} + 2\text{CO}_3^{-2} = \text{UO}_2(\text{CO}_3)_2^{-2}$	17 ^{c, d, e}
$\text{UO}_2(\text{CO}_3)_3^{-4}$	$\text{UO}_2^{+2} + 3\text{CO}_3^{-2} = \text{UO}_2(\text{CO}_3)_3^{-4}$	21.63 ^{c, d, e}
UO_2F^+	$\text{UO}_2^{+2} + \text{F}^- = \text{UO}_2\text{F}^+$	5.09 ^{a, c, e, f}
$\text{UO}_2\text{F}_2(\text{aq})$	$\text{UO}_2^{+2} + 2\text{F}^- = \text{UO}_2\text{F}_2(\text{aq})$	8.62 ^{c, e, f}
UO_2F_3^-	$\text{UO}_2^{+2} + 3\text{F}^- = \text{UO}_2\text{F}_3^-$	10.9 ^{a, c, e, f}
$\text{UO}_2\text{F}_4^{-2}$	$\text{UO}_2^{+2} + 4\text{F}^- = \text{UO}_2\text{F}_4^{-2}$	11.7 ^{a, c, e, f}
$\text{UO}_2\text{NO}_3^{+1}$	$\text{UO}_2^{+2} + \text{NO}_3^- = \text{UO}_2\text{NO}_3^{+1}$	0.3 ^e
UO_2PO_4^-	$\text{UO}_2^{+2} + \text{PO}_4^{-3} = \text{UO}_2\text{PO}_4^-$	13.25 ^{b, e}
$\text{UO}_2\text{HPO}_4(\text{aq})$	$\text{UO}_2^{+2} + \text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{HPO}_4(\text{aq})$	19.655 ^{b, e}
$\text{UO}_2\text{H}_2\text{PO}_4^+$	$\text{UO}_2^{+2} + 2\text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{H}_2\text{PO}_4^+$	22.833 ^{b, e}
$\text{UO}_2\text{H}_3\text{PO}_4^{+2}$	$\text{UO}_2^{+2} + 3\text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{H}_3\text{PO}_4^{+2}$	22.47 ^{a, e}
$\text{UO}_2(\text{H}_2\text{PO}_4)\text{H}_3\text{PO}_4^+$	$\text{UO}_2^{+2} + 5\text{H}^+ + 2\text{PO}_4^{-3} = \text{UO}_2(\text{H}_2\text{PO}_4)\text{H}_3\text{PO}_4^+$	45.058 ^{d, e}
$\text{UO}_2(\text{H}_2\text{PO}_4)_3^-$	$\text{UO}_2^{+2} + 6\text{H}^+ + 3\text{PO}_4^{-3} = \text{UO}_2(\text{H}_2\text{PO}_4)_3^-$	66.245 ^b
$\text{UO}_2\text{H}_4(\text{PO}_4)_2(\text{aq})$	$\text{UO}_2^{+2} + 4\text{H}^+ + 2\text{PO}_4^{-3} = \text{UO}_2\text{H}_4(\text{PO}_4)_2(\text{aq})$	44.7 ^b
$\text{UO}_2\text{SO}_4(\text{aq})$	$\text{UO}_2^{+2} + \text{SO}_4^{-2} = \text{UO}_2\text{SO}_4(\text{aq})$	3.18 ^b
$\text{UO}_2(\text{SO}_4)_2^{-2}$	$\text{UO}_2^{+2} + 2\text{SO}_4^{-2} = \text{UO}_2(\text{SO}_4)_2^{-2}$	4.14 ^a
$\text{UO}_2\text{H}_3\text{SiO}_4^+$	$\text{UO}_2^{+2} + \text{Si}(\text{OH})_4 = \text{UO}_2\text{H}_3\text{SiO}_4^+ + \text{H}^+$	-1.911 ^b

^a Allison et al., 1991^c Langmuir, 1997^e Grenthe et al., 1992^b Schecher, 2001^d Payne, 1999^f Giammar, 2001

Table 6-5. Surface complexation U(VI) reactions and equilibrium constants (T=25 °C, I=0).

Sediment Sample	Reaction	Log K
101B	$\text{S(OH)}_2 + \text{UO}_2^{+2} = \text{SO}_2\text{-UO}_2 + 2\text{H}^+$	7.65
Hanford Unit 1	$\text{W(OH)}_2 + \text{UO}_2^{+2} = \text{WO}_2\text{-UO}_2 + 2\text{H}^+$	1.75
104B	$\text{S(OH)}_2 + \text{UO}_2^{+2} = \text{SO}_2\text{-UO}_2 + 2\text{H}^+$	5.4
Hanford Unit 2	$\text{W(OH)}_2 + \text{UO}_2^{+2} = \text{WO}_2\text{-UO}_2 + 2\text{H}^+$	1.6
106B	$\text{S(OH)}_2 + \text{UO}_2^{+2} = \text{SO}_2\text{-UO}_2 + 2\text{H}^+$	7.45
Hanford Unit 2	$\text{W(OH)}_2 + \text{UO}_2^{+2} = \text{WO}_2\text{-UO}_2 + 2\text{H}^+$	1.5
112B	$\text{S(OH)}_2 + \text{UO}_2^{+2} = \text{SO}_2\text{-UO}_2 + 2\text{H}^+$	7.5
Plio-Pleistocene (Caliche)	$\text{W(OH)}_2 + \text{UO}_2^{+2} = \text{WO}_2\text{-UO}_2 + 2\text{H}^+$	2.5
119B	$\text{S(OH)}_2 + \text{UO}_2^{+2} = \text{SO}_2\text{-UO}_2 + 2\text{H}^+$	6.5
Upper Ringold	$\text{W(OH)}_2 + \text{UO}_2^{+2} = \text{WO}_2\text{-UO}_2 + 2\text{H}^+$	0.15
121	$\text{S(OH)}_2 + \text{UO}_2^{+2} = \text{SO}_2\text{-UO}_2 + 2\text{H}^+$	6.5
Upper Ringold	$\text{W(OH)}_2 + \text{UO}_2^{+2} = \text{WO}_2\text{-UO}_2 + 2\text{H}^+$	1.9
124	$\text{S(OH)}_2 + \text{UO}_2^{+2} = \text{SO}_2\text{-UO}_2 + 2\text{H}^+$	6.5
Ringold Unit E Gravels	$\text{W(OH)}_2 + \text{UO}_2^{+2} = \text{WO}_2\text{-UO}_2 + 2\text{H}^+$	1.65

Table 6-6. Solid U(VI) reactions and equilibrium constants (T=25 °C, I=0).

Species	Reaction	log K
Uranophane	$\text{Ca}^{+2} + 2\text{UO}_2^{+2} + 2\text{Si(OH)}_4 = \text{Ca(UO}_2)_2[\text{SiO}_3(\text{OH})]_2 \cdot 5\text{H}_2\text{O} + 6\text{H}^+$	-17.49 ^b
$\text{UO}_2(\text{OH})_2$ (beta)	$\text{UO}_2^{+2} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-5.612 ^b
Rutherfordine	$\text{UO}_2^{+2} + \text{CO}_3^{-2} = \text{UO}_2\text{CO}_3$	14.5 ^b
Autunite	$\text{Ca}^{+2} + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{Ca(UO}_2)_2(\text{PO}_4)_2$	44.7 ^a
H-Autunite	$2\text{H}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2$	48.42 ^a
K-Autunite	$2\text{K}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{K}_2(\text{UO}_2)_2(\text{PO}_4)_2$	48.244 ^b
Na-Autunite	$2\text{Na}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2$	47.6 ^a
$\text{UO}_2(\text{NO}_3)_2$	$\text{UO}_2^{+2} + 2\text{NO}_3^- = \text{UO}_2(\text{NO}_3)_2$	-12.148 ^b
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 2\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	-4.851 ^b
$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 3\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	-3.39 ^b
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 6\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	-2.046 ^b

^a Allison et al., 1991
^b Schecher, 2001

6.3.4 Description of Model Scenarios

MSE used PHREEQCI to simulate four scenarios: three different scenarios for uranium mobility, and one scenario that has direct applicability to the current leading remedial alternative for the site, i.e., capping.

In each scenario, the waste-affected recharge moved through the vadose zone to the water table where it mixed with the aquifer water; the chemical composition was based on analyses of water from well 699-55-89 (see Table 6-3). In addition to the waste and water quality data that were common for all simulations, each of the uranium mobility scenarios used specific variables, as described in the following sections.

6.3.4.1 Scenario 1—Vadose Zone to Water Table Interface

Scenario 1 (Figure 6-5) considered that the 46,200 m³ of waste disposed to the U1/U2 Cribs between 1956 and 1963 took a path thorough the entire vadose zone (i.e., the Hanford, Plio-Pleistocene, and Ringold formations) to the water table interface where it mixed with groundwater.

Figure 6-5. Uranium mobility for Scenario 1.

This scenario was used to model two “snapshots” in the waste disposal history: (a) after the first sediment-pore-volume of the waste was released to the U1/U2 Cribs, and (b) after all 46,200 m³ of waste was disposed to the cribs. In both cases, the contaminated water from the unsaturated zone recharged the aquifer at the water table 79 m (258 ft) below ground surface (bgs) and mixed with its water flowing laterally from the west.

MSE considered the following variables, which are summarized in Table 6-7 and Table 6-8, for modeling Scenario 1:

Size of the sediment column affected by advection: By definition, a 1D advection model assumes that water migrates through a column of sediment that has a uniform cross sectional area throughout its length. In this case, the cross-sectional area of the column equals the footprint of U1/U2 Cribs. In reality, however, the wastes that were disposed to U1/U2 Cribs most probably migrated downward within an

overall conical shaped sediment domain (79 m high) truncated at the top with an area equal to the footprint of U1/U2 Crib. To determine the effect of such a spread of the waste stream, MSE simulated advective transport for three columns of different cross sectional areas. These areas were equal to the horizontal projection of Crib U1/U2, i.e. 297 m² (24.4 m x 12.2 m); twice larger, i.e. 595 m² (31.2 m x 19.0 m); and four times larger, i.e. 1190 m² (41.1 m x 28.9 m).

Table 6-7. Results from PHREEQCI simulations of scenario 1. (Precipitation of solids NOT allowed.)

Simulation ID	Cross - sectional area of sediment column (m ²)	Mixing zone width (m)	Waste saturation ratio	Pore volumes of waste	Mixing ratio of aquifer water and waste	Uranium Concentration	
						At the water table (:g/L)	In the aquifer (:g/L)
1-1	297.4	12.2	0.56	1.00	0.32	18,922	14,377
1-2				11.75		76,986	58,551
1-3			0.66	1.00		19,812	15,053
1-4				10.00		76,986	58,551
1-5			0.76	1.00		21,505	16,340
1-6				8.66		76,986	58,551
1-7	594.9	19.0	0.56	1.00	0.51	18,922	12,484
1-8				5.88		77,969	51,507
1-9			0.66	1.00		19,812	13,071
1-10				5.00		78,007	51,533
1-11			0.76	1.00		21,505	14,189
1-12				4.33		77,841	51,424
1-13	1189.8	28.9	0.56	1.00	0.77	18,922	10,781
1-14				2.94		77,633	44,300
1-15			0.66	1.00		19,812	11,289
1-16				2.50		77,310	44,116
1-17			0.76	1.00		21,505	12,254
1-18				2.17		77,545	44,250

Water saturation ratio of pores conveying the waste from the Crib: For unsaturated conditions, MSE expects that the waste does not percolate through the entire cross section of the pore space, like it would have under saturated conditions. Therefore, the saturation ratio, which is defined as the ratio of saturated pore space to total pore space, was smaller than 1. On average, the unsaturated sediment column at the location of borehole 299 W19-43 contained 0.04 grams of water per one gram of sediment; and, the bulk density of sediment is 1.65 g/cm³. Therefore, the volumetric moisture content is an equal to 0.066. Assuming a total porosity of 0.3, the pore saturation ratio of the initial, unsaturated sediment is 0.22.

This saturation ratio reflects the flow conditions produced by the infiltration of atmospheric water at the rate of 80 mm/year. According to Glendon Gee (PNNL soil scientist, e-mail communication, August 28, 2003), recharge rates in the 200 West Area range from 40-80 mm/yr. U1/U2 Crib waste was disposed at the average rate ranging from 5.5 m/year to 22.1 m/year, depending on the footprint of affected sediment column. At these rates, the waste undoubtedly percolated at the higher saturation ratio than at natural conditions. However, because of the intermittent nature of the waste disposal, it is unlikely that saturated flow, expressed by the saturation ratio of 1, was established throughout the sediment column. Therefore, for the PHREEQCI modeling, which simulated time-average conditions, MSE assumed that the waste occupied 3-times the space taken by the original soil moisture, thus making the pore saturation ratio with waste 0.66. The 0.66 value for the saturation ratio was bracketed by 0.1 giving saturation ratios of 0.56 and 0.76 for the PHREEQCI modeling. Concentrations of sorbing surface sites were adjusted to match the given saturation conditions.

The unsaturated character of flow conditions for the waste is further supported by comparing the unsaturated hydraulic conductivities for the atmospheric water with that corresponding to the average waste flow rate. For the atmospheric water, the value for actual hydraulic conductivity can be presumed as equal to the infiltration rate 2.5×10^{-7} cm/s (80 mm/year) if a hydraulic gradient of 1 is assumed for simplicity. For the average flow rate of waste the corresponding hydraulic conductivity values would range from 1.7×10^{-5} cm/s (5.5 m/year) to 7×10^{-5} cm/s (22.1 m/year). It is common that unsaturated hydraulic conductivity for sandy deposits change 4 to 5 orders of magnitude between its lowest value close to the residual moisture content and its high value for the saturated flow (Feike et al 1997, Zaluski et al 2000). Considering that moisture content of 0.066, determined for samples from borehole 299-W19-43, is close to the residual moisture content for sand often evaluated as 0.04, the increase of hydraulic conductivity of two orders of magnitude places the flow conditions still within the unsaturated flow. In fact, the saturated hydraulic conductivity in the vertical direction for Ringold sediments was estimated as 1.1×10^{-3} cm/s, two orders of magnitude higher than those calculated for the average flow rates of waste.

Pore volumes of Crib U1/U2 waste: The number of pore volumes that the 46,200 m³ of waste disposed to U1/U2 Cribbs would fill are listed in Table 6-7 and Table 6-8. These pore volumes were calculated based on the above stated cross sectional areas and saturation ratios. For instance, for the 0.66 saturation ratio and the sediment column with a cross sectional area equal to the foot print U1/U2 Cribbs, the number of pore volumes of waste is 10.

Table 6-8. Results from PHREEQCI simulations of scenario 1. (Precipitation of solids allowed.)

Simulation ID	Cross - sectional area of sediment column	Mixing zone width (m)	Waste saturation ratio	Pore volumes of waste	Mixing ratio of aquifer water and waste	Uranium Concentration	
						At the water table (:g/L)	In the aquifer (:g/L)
1-1B	297.4	12.2	0.56	1.00	0.32	0.02	1.85
1-2B				11.75		0.04	0.07
1-3B			0.66	1.00		0.02	1.85
1-4B				10.00		0.04	0.07
1-5B			0.76	1.00		0.02	1.85
1-6B				8.66		0.04	0.07
1-7B	594.9	19.0	0.56	1.00	0.51	0.02	2.61
1-8B				5.88		0.04	0.09
1-9B			0.66	1.00		0.02	2.61
1-10B				5.00		0.04	0.09
1-11B			0.76	1.00		0.02	2.61
1-12B				4.33		0.04	0.09
1-13B	1189.8	28.9	0.56	1.00	0.77	0.02	3.29
1-14B				2.94		0.04	0.13
1-15B			0.66	1.00		0.02	3.29
1-16B				2.50		0.04	0.13
1-17B			0.76	1.00		0.02	3.29
1-18B				2.17		0.04	0.13

Aquifer mixing ratios: The mixing ratios of the groundwater flowing in the aquifer and contaminated recharge water from the vadose zone were 0.32, 0.51 and 0.77, for the sediment columns of the cross sectional areas 297 m², 595 m², and 1190 m², respectively. These values were calculated as a ratio of groundwater flow rate to the recharge rate of contaminated water. The groundwater flow rate (approximately 0.48 m³/day [d]) in the top 30 meters and per unit width of the aquifer, was calculated using an aquifer regional horizontal hydraulic conductivity (K_h) of 10 m/d, an aquifer groundwater hydraulic gradient (I) of 0.0016 (Poston et al, 2000), and an assumed effective aquifer thickness of 30 m. Likewise, the recharge rate from the vadose zone (per unit width of the aquifer) was calculated using the

volume of the waste ($46,200 \text{ m}^3$), the time period for the waste disposal, and the width of the respective recharge zone. The mixing ratios calculated (as described above) are the average mixing ratios calculated based on the assumed volume and time for the waste discharged to U1/U2 Cribs.

6.3.4.2 Scenario 2—Hanford Formation and then through a Window in the Caliche Layer Pushed by Water from U16 Crib

The concept for Scenario 2 is shown graphically in Figure 6-6.

Figure 6-6. Uranium mobility for Scenario 2.

Scenario 2 also starts with the $46,200 \text{ m}^3$ of waste disposed to U1/U2 Cribs between 1956 and 1963, but assumes that the waste percolated initially only through the Hanford formation. The waste accumulated on the top of the caliche portion of the Plio-Pleistocene formation at 55 m (180 ft) bgs, creating a perched zone saturated with contaminated water. The entire volume of perched water was then pushed “laterally”⁴ by the wastewater released to the adjacent the U16 Crib to a hypothetical erosional window in the caliche layer. The U1/U2 Crib waste then migrated through the Ringold formation, reacting with the sediment, to the aquifer (79 m bgs). Aquifer water, flowing laterally from the west mixed with the U1/U2 Crib waste.

Scenario 2 modeling variables (see Table 6-9 and Table 6-10) included:

Size of the Hanford sediment column affected by advection: The size of the sediment column affected by advection was assumed the same as for Scenario 1 with the exception that the waste propagated to a

⁴ This term is used here only for conceptual reasons to visualize what could have actually occurred in the field. In the modeling process, because PHREEQCI considers only one-dimensional advection, the perched water was directly introduced to Ringold sediments without passing through the caliche cells.

shallower horizon, i.e., only through the Hanford formation to the caliche, 55 m (180 ft) bgs, rather than to the water table interface, 79m (258 ft) bgs.

Table 6-9. Results from PHREEQCI simulations of scenario 2. (Precipitation of solids NOT allowed.)

Simulation ID	Cross sectional area of the sediment column (m ²)	Mixing zone width (m)	Hanford Sediments		Ringold Sediments	Mixing ratio of aquifer water and waste	Uranium Concentration	
			Waste saturation ratio	Pore volumes of waste	Pore volumes of waste		At the water table (:g/L)	In the aquifer (:g/L)
2-1	297.4	12.2	0.56	16.85	21.8	0.020	76,631	75,170
2-2			0.66	14.29			76,631	75,170
2-3			0.76	12.41			76,631	75,170
2-4	594.9	19.0	0.56	8.42	10.9	0.015	77,395	76,229
2-5			0.66	7.15			77,391	76,224
2-6			0.76	6.21			77,388	76,222
2-7	1189.8	28.9	0.56	4.21	5.4	0.012	76,817	75,891
2-8			0.66	3.57			76,926	75,998
2-9			0.76	3.10			76,962	76,036

Table 6-10. Results from PHREEQCI simulations of scenario 2. (Precipitation of solids allowed.)

Simulation ID	Cross sectional area of the sediment column (m ²)	Mixing zone width (m)	Hanford Sediments		Ringold Sediments	Mixing ratio of aquifer water and waste	Uranium Concentration	
			Waste saturation ratio	Pore volumes of waste	Pore volumes of waste		At the water table (:g/L)	In the aquifer (:g/L)
2-1B	297.4	12.2	0.56	16.85	21.8	0.020	0.99	1.00
2-2B			0.66	14.29			0.99	1.00
2-3B			0.76	12.41			0.99	1.00
2-4B	594.9	19.0	0.56	8.42	10.9	0.015	1.60	1.60
2-5B			0.66	7.15			1.60	1.60
2-6B			0.76	6.21			1.55	1.55
2-7B	1189.8	28.9	0.56	4.21	5.4	0.012	1.01	1.02
2-8B			0.66	3.57			1.01	1.02
2-9B			0.76	3.10			1.01	1.02

Water saturation ratios in Hanford sediments: The water saturation ratios of pores conveying the waste from the U1/U2 Cribs to the caliche were assumed the same as for Scenario 1. Thus, sediment was assumed to have an initial saturation ratio of 0.22. Waste moving through the sediment occupied 3-times the volume occupied by the initial sediment water resulting in a saturation ratio of 0.66. The 0.66 saturation ratio value was bracketed by 0.1 making the saturation ratios used for the model 0.56, 0.66, and 0.76. Concentrations of sorbing surface sites were adjusted to match the given saturation conditions.

Pore volumes of U1/U2 Crib waste percolating through Hanford sediments: The number of pore volumes for the waste stream percolating from the U1/U2 Cribs through Hanford sediments was calculated based on the above stated cross sectional areas and the saturation ratios. For example, for the 0.66 saturation ratio and the sediment column of the cross sectional area equal to the footprint of the U1/U2 Cribs, the number of pore volumes was 14.3.

U16 Crib mixing ratio: No mixing of the U16 Crib water with the contaminated perched water was modeled because of the uncertainty of the U16 Crib water composition and the volume of this water that might have reached the contaminated water perched under the U1/U2 Cribs. Water discharged from U16 Crib was considered as providing the hydraulic gradient to mobilize contaminated perched water and push it “laterally” toward a hypothetical window in the caliche layer.

Size of Ringold sediment column affected by advection: The size of the Ringold sediment column affected by advection after the perched water was “laterally” pushed to this sediment through a window in the caliche layer was assumed the same as for the Hanford formation, however the height of the column was only 24 m.

Water saturation ratio in Ringold Sediments: The water saturation ratio of pores conveying the waste within the Ringold sediments was assumed 1 (full saturation) as implicated by a one-time “push” by U16 Crib wastewater that was at full saturation within the perched zone.

Pore volumes of U1/U2 Cribs waste in Ringold sediments: The number of pore volumes for the waste stream percolating from the perched zone through the Ringold sediments was calculated based on the above stated cross sectional areas and a saturation ratio equal to 1, as it was in the perched zone. The calculated pore volumes were 22, 11, and 5.4 for the cross sectional areas of 297 m², 595 m², and 1190 m², respectively.

Aquifer mixing ratios: The mixing ratios of the groundwater flowing in the aquifer and the contaminated recharge water from the Ringold sediments under a hydraulic gradient of 1 are 0.020, 0.015, and 0.012 for the cross sectional areas of 297 m², 595 m², and 1190 m², respectively. These values were calculated as a ratio of groundwater flow rate to the recharge rate of wastes coming from the temporarily and locally saturated Ringold sediments. The groundwater flow rate (0.48 m³/d) was calculated the same as for Scenario 1. The recharge rate from the temporarily and locally saturated Ringold sediments was calculated assuming a vertical hydraulic conductivity (K_v) of 1 m/d, i.e., 1/10 of the K_h value, and an I equal to 1 as appropriate for the flow in the vertical (downward) direction in fully saturated medium.

6.3.4.3 Scenario 3—Hanford Formation and then through a Well Annulus to Water Table Pushed by Water from U16 Crib

Scenario 3 (see Figure 6-7) differs from Scenario 2 in that the perched contaminated water from the U1/U2 Cribs was pushed by the water released to Crib U16 to either an unidentified well where it flowed through the annulus between well casing and the sediments or to a clastic dike within the sediment, directly to the aquifer.

PHREEQC Modeling Scenario 3

Figure 6-7. Uranium mobility for Scenario 3.

The model assumes that the chemical composition of the pushed water did not change until it mixed with the aquifer water at the water table interface (79 m bgs). MSE considered the following variables (see Table 6-11 and Table 6-12) for modeling of this scenario:

Size of the Hanford sediment column affected by advection: The size of the sediment column affected by advection was assumed the same as for Scenario 2. This means that the waste from U1/U2 Cribs percolated through the Hanford formation to the caliche, 55 m (180 ft) bgs.

Water saturation ratios in Hanford sediments: The water saturation ratios of pores conveying the waste from the U1/U2 Cribs to the caliche was assumed the same as for Scenario 2. This means that the 0.66 saturation ratio (three times the initial saturation ratio value for sediments) was bracketed by 0.1 making the saturation ratios used for the model 0.56, 0.66, and 0.76. Concentrations of sorbing surface sites were adjusted to match the given saturation conditions.

Pore volumes of U1/U2 Cribs waste percolating through Hanford sediments: The number of pore volumes for the waste stream percolating from U1/U2 Cribs through Hanford sediments were assumed the same as for Scenario 2. This means that they were calculated based on the above stated cross sectional areas and the saturation ratios. For example, for the 0.66 saturation ratio and the sediment column of the cross sectional area equal to the U1/U2 Cribs the number of pore volumes was 14.3.

U16 Crib mixing ratio: No mixing of the U16 Crib water with the contaminated perched water was modeled because of the uncertainty of the U16 Crib water composition and the volume of this water that might have reached the contaminated water perched under U1/U2 Cribs. Water discharged from U16 Crib was considered as providing the hydraulic gradient to mobilize contaminated perched water and push

it “laterally” to an unidentified well where it flowed through the annulus between well casing and the sediments, or to a clastic dike within the sediment.

Aquifer mixing ratios: The mixing ratios of the groundwater flowing in the aquifer and the contaminated perched water were assumed the same as for Scenario 2. Such an assumption was made because of the PHREEQCI limitation of 1D advective transport and the lack of any data for the surmised flow through a well annulus. The mixing ratios calculated for Scenario 2 are very low, thus indicating that dilution of the recharging water by the aquifer water would be low. A similar, if not lower, dilution ratio would take place at a location where a point-source (the well annulus) released contaminated water.

Table 6-11. Results from PHREEQCI simulations of scenario 3. (Precipitation of solids NOT allowed.)

Simulation ID	Cross sectional area of the sediment column (m ²)	Mixing zone width (m)	Hanford Sediments		Mixing ratio of aquifer water and waste	Uranium Concentration	
			Waste saturation ratio	Pore volumes of waste		At the water table (:g/L)	In the aquifer (:g/L)
3-1	297.4	12.2	0.56	16.85	0.020	76,631	75,170
3-2			0.66	14.29		76,631	75,170
3-3			0.76	12.41		76,631	75,170
3-4	594.9	19.0	0.56	8.42	0.015	77,360	76,193
3-5			0.66	7.15		77,355	76,191
3-6			0.76	6.21		77,353	76,189
3-7	1189.8	28.9	0.56	4.21	0.012	76,831	75,905
3-8			0.66	3.57		76,938	76,010
3-9			0.76	3.10		76,974	76,048

Table 6-12. Results from PHREEQCI simulations of scenario 3. (Precipitation of solids allowed.)

Simulation ID	Cross sectional area of the sediment column (m ²)	Mixing zone width (m)	Hanford Sediments		Mixing ratio of aquifer water and waste	Uranium Concentration	
			Waste saturation ratio	Pore volumes of waste		At the water table (:g/L)	In the aquifer (:g/L)
3-1B	297.4	12.2	0.56	16.85	0.020	0.99	1.00
3-2B			0.66	14.29		0.99	1.00
3-3B			0.76	12.41		0.99	1.00
3-4B	594.9	19.0	0.56	8.42	0.015	1.00	1.10
3-5B			0.66	7.15		1.00	1.10
3-6B			0.76	6.21		1.00	1.10
3-7B	1189.8	28.9	0.56	4.21	0.012	1.01	1.02
3-8B			0.66	3.57		1.01	1.02
3-9B			0.76	3.10		1.01	1.02

6.3.4.4 Scenario 4—Vadose Zone to Water Table Interface and Flushing by Atmospheric Water

Scenario 4, shown in Figure 6-8, focuses on the impact infiltration of atmospheric water has on the contaminated water recharging the aquifer after the waste disposal to U1/U2 Cribs ceased and the uranium concentrations in vadose zone achieved geochemical equilibrium.

Figure 6-8. Uranium mobility for Scenario 4.

For this scenario, the aquifer water mixes with the recharging contaminated water from the vadose zone, which is being advected by the 80 mm/year effective infiltration of atmospheric water. This infiltration rate was based on information obtained from Glendon Gee (PNNL soil scientist, e-mail communication, August 28, 2003) and represents infiltration for current land surface conditions. The current remedial alternative for the site includes capping the land surface, which would likely reduce the infiltration rate to around 10 mm/year according to Glendon Gee (PNNL soil scientist, e-mail communication, August 28, 2003). Scenario 4 was simulated for the post-Scenario 1 vadose zone geochemical conditions.

Initial geochemical conditions for Scenario 4 were assumed to be the final geochemical conditions modeled in Scenario 1. MSE considered the following variables (see Table 6-13 and Table 6-14) for modeling of this scenario:

Size of the sediment column affected by advection: The size of the soil column affected by advection of atmospheric water was assumed the same as for Scenario 1.

Water saturation ratios of pores conveying atmospheric water: The water saturation ratio of pores conveying atmospheric water down to the water table interface was assumed to be 0.22, i.e., at the

volumetric moisture content measured in sediment samples collected from borehole 299-W19-43. Concentrations of sorbing surface sites were adjusted to match this pore saturation ratio.

Pore volumes of the atmospheric water: The number of pore volumes for the atmospheric water migrating from the ground surface to the water table interface is time dependant and was based on the current rate of atmospheric water infiltration (0.08 m/y). It was calculated that approximately 0.5 pore volumes of atmospheric water would enter the sediment column in the time period between 1963 (end of waste disposal to the U1/U2 Cribs) and 1996. Likewise, one pore volume would pass through the sediment column by the year 2028. Had the estimated infiltration rate for a capped site been used (0.01 m/year), one pore volume would not pass through the sediment column until around the year 2483. This means that capping the site effectively increases the time for one pore volume to pass through the sediment column by eight times.

Aquifer mixing ratios: The mixing ratios of the groundwater flowing in the aquifer and contaminated water recharging from the vadose zone would be 90, 70 and 53 for the sediment columns, with cross sectional areas of 297 m², 595 m², and 1190 m², respectively. These values were calculated as a ratio of groundwater flow rate to the recharge rate of wastes coming from the vadose zone. The groundwater flow rate (0.48 m³/d) was calculated the same as for Scenario 1. The recharge rate from the vadose zone was calculated based on the atmospheric water infiltration rate (0.00022 m/d) and the length of the recharge zone along the direction of groundwater flow.

Table 6-13. Results from PHREEQCI simulations of scenario 4. (Precipitation of solids NOT allowed.)

Simulation ID	Cross sectional area of the sediment column (m ²)	Mixing zone width (m)	Waste saturation ratio	Pore volumes of waste	Pore volumes of atmospheric water	Mixing ratio of aquifer water and atmospheric water affected by waste	Uranium Concentration	
							At the water table (:g/L)	In the aquifer (:g/L)
4-1	297.4	12.2	0.56	11.75	0.5	90	76,986	856
4-2					1		629	14
4-3			0.66	10.00	0.5		76,986	856
4-4					1		563	14
4-5			0.76	8.66	0.5		76,986	856
4-6					1		508	13
4-7	594.9	19.0	0.56	5.88	0.5	70	77,284	1,091
4-8					1		649	17
4-9			0.66	5.00	0.5		77,407	1,093
4-10					1		579	16
4-11			0.76	4.33	0.5		77,593	1,095
4-12					1		520	15
4-13	1189.8	28.9	0.56	2.94	0.5	53	77,857	1,411
4-14					1		732	21
4-15			0.66	2.50	0.5		77,405	1,403
4-16					1		651	19
4-17			0.76	2.17	0.5		77,438	1,403
4-18					1		571	18

Table 6-14. Results from PHREEQCI simulations of scenario 4. (Precipitation of solids allowed.)

Simulation ID	Cross sectional area of the sediment column (m ²)	Mixing zone width (m)	Waste saturation ratio	Pore volumes of waste	Pore volumes of atmospheric water	Mixing ratio of aquifer water and atmospheric water affected by waste	Uranium Concentration	
							At the water table (:g/L)	In the aquifer (:g/L)
4-1B	297.4	12.2	0.56	11.75	0.5	90	0.04	7.53
4-2B					1		0.01	7.53
4-3B			0.66	10.00	0.5		0.04	7.53
4-4B					1		0.02	7.53
4-5B			0.76	8.66	0.5		0.04	7.53
4-6B					1		0.02	7.53
4-7B	594.9	19.0	0.56	5.88	0.5	70	0.04	7.51
4-8B					1		0.00	7.51
4-9B			0.66	5.00	0.5		0.04	7.51
4-10B					1		0.00	7.51
4-11B			0.76	4.33	0.5		0.04	7.51
4-12B					1		0.00	7.51
4-13B	1189.8	28.9	0.56	2.94	0.5	53	0.04	7.48
4-14B					1		0.00	7.48
4-15B			0.66	2.50	0.5		0.04	7.48
4-16B					1		0.00	7.48
4-17B			0.76	2.17	0.5		0.04	7.48
4-18B					1		0.00	7.48

6.4 PHREEQCI MODELING PROCESS

The PHREEQCI modeling process included parameterization of the input data, input file assembly, and model runs and results retrieval. The models were not calibrated because there is no record of the uranium concentrations in the sediment and in sediment moisture beneath U1/U2 Cribs. The modeling results are summarized in Section 6.5 and interpreted as presented in Section 6.6.

6.4.1 Model Parameterization

The following sections describe the information/parameters that were quantified for simulation of the four uranium mobility scenarios. All modeling was completed assuming a temperature of 25 °C.

6.4.1.1 Thermodynamic Database

The PHREEQCI modeling was conducted using the same thermodynamic database used for the geochemical model calibration and validation efforts completed in FY03 (MSE 2003d).

6.4.1.2 Sediment

The sediment column was stratified (Figure 6-5 through Figure 6-8) based on information acquired while installing borehole 299-W19-43. The unsaturated zone, which was 258 feet thick, was divided into 43 cells for the PHREEQCI modeling. Each cell was 6 feet in thickness. The saturated zone was represented by one 6 foot cell denoted in the PHREEQCI input file as cell No. 47.

Total porosity for all sediments was assumed to be 0.3. A volumetric moisture content of 0.066 for the entire vadose zone was calculated from the average weight moisture content as determined for sediment

samples collected from borehole 299-W19-43. A bulk sediment density of 1.65 g/cm^3 was used for converting the weight moisture content to the volumetric moisture content.

An initial water saturation ratio of 0.22 for the unsaturated sediments was derived using the volumetric water content and the porosity ratios. Modeled saturation ratios were 0.66, 0.56 and 0.76.

Sorbent surface area (m^2/g) for each sediment was calculated as an weighted average of literature values of surface area for goethite, hematite, and magnetite with weighting factors related to the varying amounts of each mineral observed in the soils from borehole 299-W19-43. The relative amounts of each mineral were determined through petrographic analysis. Strong and weak sorbing site concentrations (mol/L) depend on sediment saturation ratios. Sorbent mass (g/L) was calculated based on CBD analysis and sediment saturation ratios. These data are summarized in Table 6-15.

6.4.1.3 Sediment Gas

Carbon dioxide (CO_2) concentrations (ppm) in the sediment gas were taken from the results of the formation gas sampling during the installation of borehole 299-W19-43 (MSE 2002a).

6.4.1.4 Formation Water

Formation water density was 1 kg/L . Dissolved constituents in moles per kilogram of solution (mol/kg) were determined from chemical analysis of moisture in samples collected from borehole 299-W19-43. Alkalinity values in mol/kg as HCO_3^{-1} were based on chemical analysis of pore water in samples collected from borehole 299-W19-43. Carbon dioxide was assumed to be in equilibrium with CO_2 in the gases phase. Values for pH were calculated using the measured CO_2 concentrations and the laboratory determined alkalinity values. These data are summarized in Table 6-16.

6.4.1.5 Waste Stream

Density of the waste was assumed to be 1.025 kg/L . Chemistry of the waste stream, including concentrations of dissolved constituents (mol/kg) and pH, were based on the Waste Inventory Report (MSE 2002c) completed by MSE. The chemistry of the waste stream is summarized in Table 6-3. The number of pore volumes of waste that advected through the sediment column was calculated using a total volume of waste (MSE 2002c), sediment porosity, sediment saturation values, and cross-sectional areas of the soil column affected by the waste.

6.4.1.6 Atmospheric Water

The chemistry of the atmospheric water, including dissolved constituents (mol/kg), was taken from USGS records. These data were multiplied by factor 6 to simulate the effect of evaporation that increases the concentration of constituents in the water that actually infiltrates (recharges) the sediment column. The results are shown in Table 6-3.

An effective infiltration rate of 80 mm/year , which was based on information from Glendon Gee (PNNL soil scientist, e-mail communication, August 28, 2003), was assumed.

Table 6-15. Sediment sorption parameters.

Sediment sample		Formation	PHREEQCI cell ID*	Surface area (m ² /g)	Sorbent								
ID	Depth (feet)				Saturation ratio for vadose zone								
					0.56		Mass** (g)	0.66		Mass** (g)	0.76		Mass** (g)
					Site concentration (mol/L)			Site concentration (mol/L)			Site concentration (mol/L)		
					Strong	Weak		Strong	Weak		Strong	Weak	
101B	21-72	Hanford Unit 1	1-11	45.29	4.60×10 ⁻⁴	1.38×10 ⁻²	16.3	3.91×10 ⁻⁴	1.17×10 ⁻²	13.8	3.39×10 ⁻⁴	1.02×10 ⁻²	12.0
104B	111-112	Hanford Unit 2	12-28	83.40	2.09×10 ⁻³	6.27×10 ⁻²	29.3	1.77×10 ⁻³	5.32×10 ⁻²	24.8	1.54×10 ⁻³	4.62×10 ⁻²	21.6
106B	171-172	Hanford Unit 2	29-30	49.40	1.57×10 ⁻³	4.72×10 ⁻²	36.9	1.33×10 ⁻³	4.00×10 ⁻²	31.3	1.16×10 ⁻³	3.48×10 ⁻²	27.2
112B	195-196	Plio-Pleistocene (Caliche)	31-34	61.24	8.18×10 ⁻⁴	2.45×10 ⁻²	16.1	6.94×10 ⁻⁴	2.08×10 ⁻²	13.7	6.02×10 ⁻⁴	1.81×10 ⁻²	11.9
119B	231-232	Upper Ringold	35-40	143.82	1.07×10 ⁻³	3.20×10 ⁻²	37.8	9.06×10 ⁻⁴	2.72×10 ⁻²	32.1	7.87×10 ⁻⁴	2.36×10 ⁻²	27.9
121	247-249	Upper Ringold	41-43	57.61	1.48×10 ⁻³	4.45×10 ⁻²	37.0	1.26×10 ⁻³	3.78×10 ⁻²	31.4	1.09×10 ⁻³	3.28×10 ⁻²	27.3
124	272-274	Ringold Unit E Gravels (saturated)	47	63.43	8.47×10 ⁻⁴	2.54×10 ⁻²	21.1	Note: Saturation ratio for sample 124 was always 1 because the sample was in the saturated zone.					
* Each cell is 6 ft in thickness													
** Mass is an equivalent of solid concentration in g/L of solution for MINEOL+ modeling													

Table 6-16. Chemical composition of formation water.

		Concentration (mol/L)						
Sediment sample ID		101B	104B	106B	112B	119B	121	124
Depth (feet)		21-72	111-112	171-172	195-196	231-232	247-249	272-274
Formation		Hanford Unit 1	Hanford Unit 2	Hanford Unit 2	Plio-Pleistocene (Caliche)	Upper Ringold	Upper Ringold	Ringold Unit E Gravels (saturated)
PHREEQCI cell ID		1-11	12-28	29-30	31-34	35-40	41-43	47
Solution composition	Al ⁺³	9.60×10 ⁻⁷	9.60×10 ⁻⁷	9.60×10 ⁻⁷	9.60×10 ⁻⁷	9.60×10 ⁻⁷	9.60×10 ⁻⁷	5.56×10 ⁻⁶
	Ca ⁺²	2.04×10 ⁻⁴	3.79×10 ⁻⁴	9.07×10 ⁻⁴	5.09×10 ⁻⁴	7.91×10 ⁻⁵	1.01×10 ⁻⁴	8.16×10 ⁻⁴
	Fe ⁺³	3.50×10 ⁻⁷	3.50×10 ⁻⁷	3.50×10 ⁻⁷	3.50×10 ⁻⁷	3.50×10 ⁻⁷	3.50×10 ⁻⁷	1.93×10 ⁻⁶
	K ⁺	1.00×10 ⁻⁴	1.24×10 ⁻⁴	1.33×10 ⁻⁴	8.70×10 ⁻⁵	4.40×10 ⁻⁵	5.50×10 ⁻⁵	1.09×10 ⁻⁴
	Mg ⁺²	8.43×10 ⁻⁵	2.09×10 ⁻⁴	4.60×10 ⁻⁴	4.20×10 ⁻⁴	6.58×10 ⁻⁵	6.21×10 ⁻⁵	5.18×10 ⁻⁴
	Mn ⁺²	5.00×10 ⁻⁸	5.00×10 ⁻⁸	5.00×10 ⁻⁸	5.00×10 ⁻⁸	5.00×10 ⁻⁸	5.00×10 ⁻⁸	9.10×10 ⁻⁸
	N ⁺⁵	1.34×10 ⁻³	9.64×10 ⁻⁴	7.92×10 ⁻³	3.05×10 ⁻³	1.01×10 ⁻³	1.37×10 ⁻³	7.08×10 ⁻⁵
	Na ⁺	9.21×10 ⁻⁴	7.64×10 ⁻⁴	1.27×10 ⁻³	6.62×10 ⁻⁴	2.87×10 ⁻⁴	3.64×10 ⁻⁴	4.65×10 ⁻⁴
	UO ₂ ⁺²	2.51×10 ⁻⁷	8.70×10 ⁻⁸	4.00×10 ⁻⁸	5.53×10 ⁻⁷	9.00×10 ⁻⁸	8.70×10 ⁻⁸	3.20×10 ⁻⁸
	F ⁻	2.32×10 ⁻⁵	2.05×10 ⁻⁵	1.74×10 ⁻⁵	3.79×10 ⁻⁵	1.53×10 ⁻⁵	1.37×10 ⁻⁵	1.58×10 ⁻⁵
	PO ₄ ⁻³	3.87×10 ⁻⁶	2.58×10 ⁻⁶	4.84×10 ⁻⁶	6.50×10 ⁻⁷	4.20×10 ⁻⁶	4.20×10 ⁻⁶	3.79×10 ⁻⁷
	SO ₄ ⁻²	2.05×10 ⁻⁴	3.65×10 ⁻⁴	5.64×10 ⁻⁴	3.02×10 ⁻⁴	6.26×10 ⁻⁵	5.41×10 ⁻⁵	4.38×10 ⁻⁵
	H ₃ SiO ₄	7.21×10 ⁻⁴	7.21×10 ⁻⁴	7.21×10 ⁻⁴	7.21×10 ⁻⁴	7.21×10 ⁻⁴	7.21×10 ⁻⁴	7.21×10 ⁻⁴
	Alkalinity as HCO ₃	1.10×10 ⁻³	1.01×10 ⁻³	1.25×10 ⁻³	1.32×10 ⁻³	2.70×10 ⁻⁴	3.10×10 ⁻⁴	1.98×10 ⁻³
pH		7.10	6.45	6.84	6.92	6.47E+00	6.8	7.95
pe*		5.70	6.24	6.91	6.43	7.22E+00	7.78	6.3

* This was an initial pe value allowed to stabilize at the value in equilibrium with atmospheric oxygen partial pressure -0.68 (a log value)

6.4.1.7 Mixing Ratios

The mixing ratios of groundwater flowing in the aquifer (cell 47) to contaminated water recharging from the vadose zone were calculated based on groundwater flux through a unit width of the top 30 m of the aquifer and the recharge from the vadose zone at the water table interface. Recharge at the water table interface is a function of the vertical flow rate and differs for each size of the sediment column and for each Scenario. In addition, the mixing ratio depends on the length of the groundwater path beneath the sediment column. Mixing ratios used for the PHREEQCI modeling (Table 6-7 through Table 6-14) varied from 0.012 to 90.

6.4.1.8 Equilibrium Phases

The model considered equilibrium phases with calcite, aluminum hydroxide, carbon dioxide, and selected uranium compounds. These uranium compounds are listed in Table 6-6. No pure phases, with the exception of calcite in the caliche layer, were initially present in the model. The caliche layer was modeled as having an “infinite” amount of calcite. This was done by setting the initial amount of calcite present to 10 mols.

Each modeling scenario was simulated twice. First, saturation indices (SI) for uranium compounds (Table 6-6) were set to 20, disallowing precipitation of these solids. This implied that the kinetics of equilibrium conditions are slow and precipitation did not happen within the time frame simulated. These simulations are identified by I.D. numbers from 1-1 to 4-18 and listed in Table 6-7, Table 6-9, Table 6-11, and Table 6-13.

In the second set of simulations, SI values were set to 0, allowing the uranium compounds to precipitate. These simulations are identified by I.D. numbers from 1-1B to 4-18B and listed in Table 6-8, Table 6-10, Table 6-12, and Table 6-14.

The SI value for aluminum hydroxide was always kept as zero.

6.4.1.9 Pore Volumes Transferred

There was no difference in the number of pore volumes transferred for the simulations that disallow uranium precipitation and those that precipitated uranium, with an exception for Scenario 4. In that scenario with uranium precipitating, 10 pore volumes of atmospheric water were used instead of one.

6.4.2 Input File Structure

A PHREEQCI input file is built around the keywords describing geochemical processes or computational procedures. The following keywords were used for the modeling: SOLUTION, EQUILIBRIUM_PHASES, SURFACE, ADVECTION, MIX, REACTION, TITLE, SELECTED_OUTPUT, USER_PUNCH, SAVE, USE and END.

The input file structures for Scenarios 1 through 4 are presented in Figure 6-9 through Figure 6-12, respectively.

Figure 6-9. PHREEQC file input structure for Scenario 1.

Figure 6-10. PHREEQCI file input structure for Scenario 2.

Figure 6-11. PHREEQC file input structure for Scenario 3.

Figure 6-12. PHREEQC file input structure for Scenario 4.

6.5 GEOCHEMICAL MODEL RESULTS

Results of the PHREEQCI geochemical modeling are included in Table 6-7 through Table 6-13. These data of uranium concentrations are presented for two locations within the modeled uranium-mobility paths, (1) at the water table in the Ringold formation, and (2) after mixing with the Ringold aquifer groundwater. Uranium concentration values shown with 5 significant digits reflect the exact modeling results rather than imply the accuracy of the uranium concentration prediction. Modeling results can be summarized by the following:

- Results of simulations for scenarios that disallow uranium precipitation differ significantly from the simulations with uranium precipitating.
- The highest final concentrations of uranium in the aquifer are reported for Scenarios 2 and 3 that disallow uranium precipitation. Concentrations are around 75,000 µg/L.
- With regard to the simulations that **DO NOT** allow uranium precipitation:
 - For Scenarios 1, 2, and 3, concentrations of uranium at the water table interface are similar.
 - Uranium concentrations in the aquifer for Scenarios 2 and 3 are about 20,000 µg/L higher than in Scenario 1. All concentrations are of the magnitude observed in the groundwater in 1986, but the concentrations for Scenarios 2 and 3 are closer.
 - The lower uranium concentration in groundwater for Scenario 1 is related to the high mixing ratio of the aquifer water and the wastewater.
 - Assuming the average concentration of uranium in the waste disposed to the U1/U2 Cribs (MSE, 2002c) was 77,122 µg/L (3.24×10^{-4} mol/L), final uranium concentration values for Scenarios 2 and 3 represent a transfer of uranium from the waste to groundwater of about 97.5%.
 - Concentrations of uranium at the water table interface are also high for Scenarios 2 and 3. These concentrations are at least 76,631 µg/L and represent a uranium transfer of approximately 99.4% from the U1/U2 Cribs waste to the water table.
 - The small difference between uranium concentrations at the water table interface and in the aquifer for Scenarios 2 and 3 is the result of a low mixing ratio of groundwater with the waste-contaminated water, the latter recharging groundwater at saturated flow conditions.
 - Final uranium concentrations for Scenario 1 fall into two ranges, 44,250 µg/L to 58,551 µg/L and 10,781 µg/L to 16,340 µg/L. These represent transfers of multi-pore volumes and a single pore volume of U1/U2 Crib waste, respectively.
 - The concentration of uranium at the water table interface for Scenario 1 ranged from 77,310 µg/L to 78,007 µg/L when more than one pore volume of waste advected through the soil column. These concentrations are slightly higher than the uranium concentration in the U1/U2 Cribs waste (77,120 µg/L).
 - As indicated by high uranium concentration at the water table interface for all simulations conducted for multi-pore volume waste transfer for Scenario 1, the buffering capacity of the soil column was exhausted within two pore volume advectations.

- In Scenario 1, simulations with advection of only one pore volume of waste, uranium concentrations at the water table interface appear independent of the footprint of the soil column but increase as the saturation ratio increases.
- In Scenario 4, uranium concentrations at the water table interface after advection of half a pore volume of atmospheric water are the same as those calculated for Scenario 1 for a multi-pore volume advection of the waste. However, the resulting uranium concentrations in the aquifer are 1 to 2 orders of magnitude lower in Scenario 4 than in Scenario 1. This is a result of the higher mixing ratio of groundwater to recharge water (atmospheric water) in Scenario 4.
- After one pore volume of atmospheric water advected through the soil column in Scenario 4, the uranium concentration at the water table drops dramatically (508 $\mu\text{g/L}$ to 732 $\mu\text{g/L}$). This decrease is the result of the “piston flow” of clean atmospheric water replacing the contaminated water. As discussed in Section 6.3.4.4, the time it would take for one pore volume of atmospheric water to move through the soil column depends on the infiltration rate. Infiltration rate would be decreased if a cap were placed over the land surface.
- With regard to the simulations that **DO** allow uranium precipitation:
 - All simulations for each scenario result in very low concentrations of uranium in the groundwater. The concentrations are several orders of magnitude lower than that observed in groundwater in 1986.
 - Uranium concentrations are, in most cases, lower than background values observed in the porewater samples from borehole 299-W19-43. The disparity results from the diverse chemistry between the wastewater and porewater.
 - Uranium is removed from the solution through precipitation of sodium autunite in the first cell of the model. The amount of this precipitate increases with each pore volume transferred through the cell.
 - Although final aqueous uranium concentrations at the water table interface are less than 1 mg/L after 10 pore volumes of atmospheric water had been transferred in Scenario 4, uranium concentrations in the pore water of the upper section of the sediment column increased with each pore volume transferred through the sediment.

6.6 GEOCHEMICAL MODEL DISCUSSION/CONCLUSIONS

6.6.1 Interpretation of the Results

When U(VI) solids, specifically sodium autunite, are allowed to precipitate the concentrations of uranium in the groundwater are extremely low and do not correlate with historical uranium concentrations. This suggests that the kinetics of sodium autunite formation may be an important factor to consider. PHREEQCI is an equilibrium model and therefore cannot account for kinetics. Modeling results suggest the kinetics of sodium autunite formation would not allow sodium autunite to reach chemical equilibrium for the geochemical conditions under the U1/U2 Cribs.

Aquifer uranium concentrations obtained from the models that do not allow U(VI) solid precipitation were more consistent with the uranium concentrations observed in groundwater in 1986. These results suggest that the waste flowing through the soil column to the groundwater was likely over saturated with

respect to uranium. Although the modeling results did not identify the exact route of uranium to the groundwater, the models demonstrate that the groundwater uranium contamination is caused by percolation of the highly concentrated and oversaturated with uranium wastewater, rather than by leaching from the uranium precipitate. The higher groundwater uranium concentrations with uranium not allowed to precipitate in Scenarios 2 and 3, where the waste "bypassed" the caliche, suggest that one of these two scenarios may more likely have occurred.

In the simulations that do not allow precipitation, adsorption of uranium becomes the controlling factor for uranium partitioning. However, the dramatic difference in results between the models that do allow precipitation and those that do not suggest that the kinetics of sodium autunite precipitation could control the transport of uranium in the concentrated waste solution.

Results indicate that the presence of a large solid phase uranium source (e.g., sodium autunite precipitate), which could be mobilized in the future, is unlikely. Results indicate that uranium could be bound up in the soil due to surface complexation processes. This premise of uranium partitioning is a vital part of any remediation plan for the U1/U2 Cribs and could be confirmed through sampling and analysis of the soil column beneath the U1/U2 Cribs.

6.6.2 Implications for the Remedial Scenarios

As the results from Scenario 4 showed (see Section 6-5), one pore volume of atmospheric water moving through the contaminated soil column could "flush" the mobile uranium from the sediment column. As a result, the remaining uranium source for the groundwater plume could be removed from the soil column around the year 2028. Assuming that the front of the oversaturated wastewater percolating through the vadose zone has already reached the water table and is being "pushed" by the infiltrating atmospheric water, capping of the surface to reduce the infiltration rate to 10 mm/year would extend the contamination problem into the future, i.e. to year 2483 as explained in Section 6.3.4.4. However, the mixing ratio of the aquifer water and the contaminated recharge to the groundwater would increase, further diluting the contaminated water.

An aggressive remedial approach would be flushing the vadose zone by introducing clean water (e.g., Columbia River water) into the soil column beneath the U1/U2 Cribs. An array of wells, surrounding the U1/U2 Cribs, would be needed to capture the contaminated groundwater until the vadose zone is completely flushed. The volume of water needed for such an operation would likely be similar to that of the disposed wastes (i.e. approximately 50,000 m³).

Another potential remedial approach to remove uranium from the unsaturated zone, as described above, is a solution mining technique. For example, the addition of phosphate to the flushing water could mobilize the uranium that is sorbed to the sediment solid phase. Again, an array of wells around the U1/U2 Cribs would be needed to capture the contaminated groundwater. The geochemical reactions resulting from the addition of phosphate, or some other lixiviant, would likely accelerate the mobilization of the uranium. As a result, a smaller volume of "flushing" solution would be needed and the pumping operation to capture the contaminated groundwater would take less time.

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APPENDIX A

Duratek Geophysical Logging Reports

Neutron-Neutron Moisture Borehole Survey Duratek Federal Services

Log Header

Project: 200 UP1

Well: 299-W19-43

Log Type: Moisture Gauge

Borehole Information

Well # <u>C3381</u>	Water Depth <u>none</u> ft	Total Depth <u>255</u> ft
Elevation Reference <u>n/a</u>	Elevation <u>n/a</u> ft	
Depth Reference <u>Ground Surface</u>	Casing Stickup <u>3.7</u> ft	
Casing Diameter <u>10.75 ID</u> in	Depth Interval <u>0 to 50</u> ft	Thickness <u>0.50</u> in
Casing Diameter <u>7.625 ID</u> in	Depth Interval <u>0 to 255</u> ft	Thickness <u>0.50</u> in

Logging Information

Log Type:	Moisture Gauge		
Company	Duratek Federal Services		
Date/Archive File Name	July 16, 2001	M2W19043	
Logging Engineers	<u>J. Kiesler</u>	<u>J. Meisner</u>	
Instrument Series	RLSM00.0		
Logging Unit	RLS-1		
Depth Interval	45 to 150 ft	Prefix	MA98
	130 to 230 ft		MA99
	225 to 255 ft		MC00
Instrument Calibration Date	July 11, 2001		
Calibration Report	WHC-SD-EN-TI-306, Rev. 0		

Analysis Information

Company	Three Rivers Scientific
Analyst	Russ Randall
Date	July 18, 2001
Notes	<u>Moisture values range from 3% to 16% for the depths logged. No valid calibration is available for the 11 inch casing diameter from surface to 50 feet. Casing thickness (0.5") applied to depths logged.</u>

RLS Neutron-Neutron Moisture

Duratek Federal Services

Project: 200 UP1

Log Date : July 15&16, 2001

Borehole: 299-W19-43

Depth Datum : Ground Surface

Analysis by Three Rivers Scientific

RLS Neutron-Neutron Moisture

Duratek Federal Services

Project: 200 UP1

Log Date : July 15&16, 2001

Borehole: 299-W19-43

Depth Datum : Ground Surface

Analysis by Three Rivers Scientific

RLS Neutron-Neutron Moisture

Duratek Federal Services

Project: 200 UP1

Log Date : July 15&16, 2001

Borehole: 299-W19-43

Depth Datum : Ground Surface

Analysis by Three Rivers Scientific

Moisture Log Analysis & Summary
Duratek Federal Services

Project: 200 UP1 Well ID: 299-W19-43
Log Type: Moisture Gauge Log Date: July 15&16, 2000

General Notes:

The 8 inch calibration coefficients were used for all logged depths. The 8 inch calibration standard has an 8.64 inch borehole diameter, with .32 inch casing thickness, and the borehole diameter in these log data is 8.625 inches. The depth interval from 0 to 50 feet has both the 8 inch and 10 inch casing. No calibration exists for the 10 inch casing.

Log data were collected with a depth reference of ground surface.

System Performance Verify: The pre- and post-log verification passed performance standards, 0.3% change from start of log to end of log, in the shield verify.

Repeat Interval: Based on the repeat interval from 130 to 150 feet and 225 to 230 feet, the logging system performed according to specifications.

Environmental Corrections: The moisture levels have been corrected for casing thickness (0.5 inch) for all well depths logged. No formation density correction has been applied because density values are not available.

Observations:

The moisture levels show values ranging from 3% to 16% for the depth interval from 50 feet to 255 feet.

A variable moisture structure shows from 75 to 255 feet. Over this depth interval, there is some correlation with the gross gamma signature, and sections with little correlation. Therefore, moisture content is sensitive to physical geologic conditions, while radionuclides variations are representative of mineralogy.

RLS Spectral Gamma Ray Borehole Survey

Duratek Federal Services

Log Header

Project: 200 UP1

Well: 299-W19-43

Log Type: HPGe Spectral Gamma Ray

Borehole Information

Well # <u>C3381</u>	Water Depth <u>none</u> ft	Total Depth <u>255</u> ft
Elevation Reference <u>n/a</u>	Elevation <u>n/a</u> ft	
Depth Reference <u>Ground Surface</u>	Casing Stickup <u>3.7</u> ft	
Casing Diameter <u>10.75 ID</u>	inDepth Interval <u>0 to 50</u> ft	Thickness <u>0.5</u> in
Casing Diameter <u>7.625 ID</u>	inDepth Interval <u>0 to 255</u> ft	Thickness <u>0.5</u> in

Logging Information

Log Type:	HPGe Spectral Gamma Ray	
Company	Duratek Federal Services	
Date/Archive File Name	July 16, 2001	H2W19043
Logging Engineers	<u>J. Meisner</u>	<u>J. Kiesler</u>
Instrument Series	RLSG07000S00.0	
Logging Unit	RLS-1	
Depth Interval	48 to 181 ft	Prefix A726
	171 to 255 ft	A727
Instrument Calibration Date	Oct 6, 2000	
Calibration Report	WHC-SD-EN-TI-292, Rev 0.	

Analysis Information

Company	Three Rivers Scientific
Analyst	Russ Randall
Date	July 18, 2001
Notes	<u>No man-made contamination detected. The natural uranium levels are slightly higher than normal Hanford soils.</u>

RLS Spectral Gamma Ray Borehole Survey

Duratek Federal Services

Project: 200 UP1

Log Date: July 16, 2001

Borehole: 299-W19-43

Naturally Occurring Radionuclides

Analysis by: Three Rivers Scientific

RLS Spectral Gamma Ray Borehole Survey

Duratek Federal Services

Project: 200 UP1

Log Date: July 16, 2001

Borehole: 299-W19-43

Naturally Occurring Radionuclides

Analysis by: Three Rivers Scientific

RLS Spectral Gamma Ray Borehole Survey

Duratek Federal Services

Project: 200 UP1

Log Date: July 16, 2001

Borehole: 299-W19-43

Naturally Occurring Radionuclides

Analysis by: Three Rivers Scientific

RLS Spectral Gamma Ray Borehole Survey

Duratek Federal Services

Project: 200 UP1

Log Date: July 16, 2001

Borehole: 299-W19-43

Naturally Occurring Radionuclides
Stacked

Analysis by: Three Rivers Scientific

RLS Spectral Gamma Ray Borehole Survey

Duratek Federal Services

Project: 200 UP1

Log Date: July 16, 2001

Borehole: 299-W19-43

Naturally Occurring Radionuclides
Stacked

Analysis by: Three Rivers Scientific

RLS Spectral Gamma Ray Borehole Survey

Duratek Federal Services

Project: 200 UP1

Log Date: July 16, 2001

Borehole: 299-W19-43

Naturally Occurring Radionuclides
Stacked

Analysis by: Three Rivers Scientific

Spectral Gamma Ray Log Analysis & Summary
Duratek Federal Services

Project: 200 UP1
Log Type: HPGe Spectral Gamma Ray

Well: 299-W19-43
Log Date: July 16, 2001

General Notes:

Total gamma is a response to geologic concentrations of natural radionuclides. A change in sensitivity of gross gamma to geologic concentrations of natural radionuclides occurs at dual casing change to single casing (50 ft).

Log data collected with a depth reference of ground surface.

System Performance Verify: The pre- and post-log verification passed performance standards; -3.5% and 2.3% changes were observed in the gross for each series run. The FWHM of the 583 keV photo peak was also within specifications for pre- and post-log verification.

Repeat Interval: Based on the repeat interval, the logging system performed as per specifications, for potassium and thorium (see notes below on radon pumping).

Environmental Corrections: All radionuclide concentrations have been corrected for casing attenuation (entire well). No water correction was applied, because water level was not reached. No casing correction was applied to the total gamma due to Compton downscatter interference.

Radionuclides:

No man-made radionuclide contamination was detected. This observation was confirmed using a summing technique for the spectral data. A stacking of spectra was performed to enhance the statistical precision of the KUT signals. Four adjacent spectra are summed and the depth is set at the mid-point of the beginning and ending spectra. This averages spectra over 2 feet vertical depth resolution, which is close to the inherent depth resolution of the gamma instrument. The next sum is performed over the 2nd through 5th spectra. Data processing is then performed over these summed spectra as normal.

The natural uranium concentration is slightly higher than normally observed for Hanford soils. No disequilibrium below radon, in the natural uranium series was observed within statistical uncertainty of the collected data. There is some indication of radon pumping causing real changes in uranium and gross. The repeat section experienced 1 hour and 18 minutes delay while refilling the tool with liquid nitrogen. Over this time interval, the uranium and gross did not repeat within statistical precision, but the potassium and thorium did repeat within statistical precision.

The changes in gross gamma from 150 to 255 feet are reflected by changes in potassium, uranium, and thorium; which is indicative of geologic effects. A stack plot is also included. The enhanced statistical precision of the stacked response allows a better view of the changes in KUT causing the changes in gross.

APPENDIX B

Reactions Used in Geochemical Modeling

Table B-1. Aqueous Reactions Used in Geochemical Modeling (T=25 °C, I=0).

Species	Reaction	log K
UO_2OH^+	$\text{UO}_2^{+2} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.2 ^{a, c, d, e, f}
$\text{UO}_2(\text{OH})_2$	$\text{UO}_2^{+2} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-11.5 ^f
$\text{UO}_2(\text{OH})_3^-$	$\text{UO}_2^{+2} + 3\text{H}_2\text{O} = \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	-19.4 ^e
$\text{UO}_2(\text{OH})_4^{-2}$	$\text{UO}_2^{+2} + 4\text{H}_2\text{O} = \text{UO}_2(\text{OH})_4^{-2} + 4\text{H}^+$	-33 ^{a, d, e, f}
$(\text{UO}_2)_2\text{OH}^{+3}$	$2\text{UO}_2^{+2} + \text{H}_2\text{O} = (\text{UO}_2)_2\text{OH}^{+3} + \text{H}^+$	-2.8 ^{d, e}
$(\text{UO}_2)_2(\text{OH})_2^{+2}$	$2\text{UO}_2^{+2} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{+2} + 2\text{H}^+$	-5.63 ^e
$(\text{UO}_2)_3(\text{OH})_4^{+2}$	$3\text{UO}_2^{+2} + 4\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_4^{+2} + 4\text{H}^+$	-11.9 ^{a, d, e, f}
$(\text{UO}_2)_3(\text{OH})_5^+$	$3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55 ^{c, e, f}
$(\text{UO}_2)_3(\text{OH})_7^-$	$3\text{UO}_2^{+2} + 7\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-31 ^{a, c, d, e, f}
$(\text{UO}_2)_4(\text{OH})_7^+$	$4\text{UO}_2^{+2} + 7\text{H}_2\text{O} = (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-21.9 ^{a, c, e, f}
$\text{UO}_2\text{CO}_3 \text{ (aq)}$	$\text{UO}_2^{+2} + \text{CO}_3^{-2} = \text{UO}_2\text{CO}_3 \text{ (aq)}$	9.67 ^{c, e}
$\text{UO}_2 (\text{CO}_3)_2^{-2}$	$\text{UO}_2^{+2} + 2\text{CO}_3^{-2} = \text{UO}_2 (\text{CO}_3)_2^{-2}$	17 ^{c, d, e}
$\text{UO}_2 (\text{CO}_3)_3^{-4}$	$\text{UO}_2^{+2} + 3\text{CO}_3^{-2} = \text{UO}_2 (\text{CO}_3)_3^{-4}$	21.63 ^{c, d, e}
UO_2F^+	$\text{UO}_2^{+2} + \text{F}^- = \text{UO}_2\text{F}^+$	5.09 ^{a, c, e, f}
$\text{UO}_2\text{F}_2 \text{ (aq)}$	$\text{UO}_2^{+2} + 2\text{F}^- = \text{UO}_2\text{F}_2 \text{ (aq)}$	8.62 ^{c, e, f}
UO_2F_3^-	$\text{UO}_2^{+2} + 3\text{F}^- = \text{UO}_2\text{F}_3^-$	10.9 ^{a, c, e, f}
$\text{UO}_2\text{F}_4^{-2}$	$\text{UO}_2^{+2} + 4\text{F}^- = \text{UO}_2\text{F}_4^{-2}$	11.7 ^{a, c, e, f}
$\text{UO}_2\text{NO}_3^{+1}$	$\text{UO}_2^{+2} + \text{NO}_3^- = \text{UO}_2\text{NO}_3^{+1}$	0.3 ^e
UO_2PO_4^-	$\text{UO}_2^{+2} + \text{PO}_4^{-3} = \text{UO}_2\text{PO}_4^-$	13.25 ^{b, e}
$\text{UO}_2\text{HPO}_4 \text{ (aq)}$	$\text{UO}_2^{+2} + \text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{HPO}_4 \text{ (aq)}$	19.655 ^{b, e}
$\text{UO}_2\text{H}_2\text{PO}_4^+$	$\text{UO}_2^{+2} + 2\text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{H}_2\text{PO}_4^+$	22.833 ^{b, e}
$\text{UO}_2\text{H}_3\text{PO}_4^{+2}$	$\text{UO}_2^{+2} + 3\text{H}^+ + \text{PO}_4^{-3} = \text{UO}_2\text{H}_3\text{PO}_4^{+2}$	22.47 ^{a, e}
$\text{UO}_2(\text{H}_2\text{PO}_4)\text{H}_3\text{PO}_4^+$	$\text{UO}_2^{+2} + 5\text{H}^+ + 2\text{PO}_4^{-3} = \text{UO}_2(\text{H}_2\text{PO}_4)\text{H}_3\text{PO}_4^+$	45.058 ^{d, e}
$\text{UO}_2(\text{H}_2\text{PO}_4)_3^-$	$\text{UO}_2^{+2} + 6\text{H}^+ + 3\text{PO}_4^{-3} = \text{UO}_2(\text{H}_2\text{PO}_4)_3^-$	66.245 ^b
$\text{UO}_2\text{H}_4(\text{PO}_4)_2 \text{ (aq)}$	$\text{UO}_2^{+2} + 4\text{H}^+ + 2\text{PO}_4^{-3} = \text{UO}_2\text{H}_4(\text{PO}_4)_2 \text{ (aq)}$	44.7 ^b
$\text{UO}_2\text{SO}_4 \text{ (aq)}$	$\text{UO}_2^{+2} + \text{SO}_4^{-2} = \text{UO}_2\text{SO}_4 \text{ (aq)}$	3.18 ^b
$\text{UO}_2 (\text{SO}_4)_2^{-2}$	$\text{UO}_2^{+2} + 2\text{SO}_4^{-2} = \text{UO}_2 (\text{SO}_4)_2^{-2}$	4.14 ^a
$\text{UO}_2\text{H}_3\text{SiO}_4^+$	$\text{UO}_2^{+2} + \text{Si}(\text{OH})_4 = \text{UO}_2\text{H}_3\text{SiO}_4^+ + \text{H}^+$	-1.911 ^b
OH^-	$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$	-13.997 ^b
AlOH^{+2}	$\text{Al}^{+3} + \text{H}_2\text{O} = \text{AlOH}^{+2} + \text{H}^+$	-4.997 ^b
$\text{Al}(\text{OH})_2^+$	$\text{Al}^{+3} + 2\text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	-10.094 ^b
$\text{Al}(\text{OH})_3 \text{ (aq)}$	$\text{Al}^{+3} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 \text{ (aq)} + 3\text{H}^+$	-16.791 ^b

Table B-1. Aqueous Reactions Used in Geochemical Modeling (T=25 °C, I=0).

Species	Reaction	log K
$\text{Al}(\text{OH})_4^-$	$\text{Al}^{+3} + 4\text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + 4\text{H}^+$	-22.688 ^b
AlF^{+2}	$\text{Al}^{+3} + \text{F}^- = \text{AlF}^{+2}$	7 ^b
AlF_2^+	$\text{Al}^{+3} + 2\text{F}^- = \text{AlF}_2^+$	12.6 ^b
$\text{AlF}_3(\text{aq})$	$\text{Al}^{+3} + 3\text{F}^- = \text{AlF}_3(\text{aq})$	16.7 ^b
AlF_4^-	$\text{Al}^{+3} + 4\text{F}^- = \text{AlF}_4^-$	19.4 ^b
AlSO_4^+	$\text{Al}^{+3} + \text{SO}_4^{-2} = \text{AlSO}_4^+$	3.89 ^b
$\text{Al}(\text{SO}_4)_2^-$	$\text{Al}^{+3} + 2\text{SO}_4^{-2} = \text{Al}(\text{SO}_4)_2^-$	4.92 ^b
CaOH^+	$\text{Ca}^{+2} + \text{H}_2\text{O} = \text{CaOH}^+ + \text{H}^+$	-12.78 ^b
$\text{CaCO}_3(\text{aq})$	$\text{Ca}^{+2} + \text{CO}_3^{-2} = \text{CaCO}_3(\text{aq})$	3.22 ^b
CaHCO_3^+	$\text{Ca}^{+2} + \text{CO}_3^{-2} + \text{H}_2\text{O} = \text{CaHCO}_3^+ + \text{OH}^-$	11.44 ^b
CaF^+	$\text{Ca}^{+2} + \text{F}^- = \text{CaF}^+$	1.038 ^b
CaNO_3^+	$\text{Ca}^{+2} + \text{NO}_3^- = \text{CaNO}_3^+$	0.5 ^b
CaPO_4^-	$\text{Ca}^{+2} + \text{PO}_4^{-3} = \text{CaPO}_4^-$	6.46 ^b
$\text{CaHPO}_4(\text{aq})$	$\text{Ca}^{+2} + \text{PO}_4^{-3} + \text{H}_2\text{O} = \text{CaHPO}_4(\text{aq}) + \text{OH}^-$	15.035 ^b
$\text{CaH}_2\text{PO}_4^+$	$\text{Ca}^{+2} + \text{PO}_4^{-3} + 2\text{H}_2\text{O} = \text{CaH}_2\text{PO}_4^+ + 2\text{OH}^-$	20.923 ^b
$\text{CaSO}_4(\text{aq})$	$\text{Ca}^{+2} + \text{SO}_4^{-2} = \text{CaSO}_4(\text{aq})$	2.36 ^b
FeOH^+	$\text{Fe}^{+2} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+$	-9.5 ^b
$\text{Fe}(\text{OH})_2(\text{aq})$	$\text{Fe}^{+2} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-20.57 ^b
$\text{Fe}(\text{OH})_3^-$	$\text{Fe}^{+2} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3^- + 3\text{H}^+$	-31 ^b
$\text{FeCO}_3(\text{aq})$	$\text{Fe}^{+2} + \text{CO}_3^{-2} = \text{FeCO}_3(\text{aq})$	5.5 ^b
$\text{Fe}(\text{CO}_3)_2^{-2}$	$\text{Fe}^{+2} + 2\text{CO}_3^{-2} = \text{Fe}(\text{CO}_3)_2^{-2}$	7.1 ^b
FeHCO_3^+	$\text{Fe}^{+2} + \text{CO}_3^{-2} + \text{H}_2\text{O} = \text{FeHCO}_3^+ + \text{OH}^-$	12.33 ^b
$\text{FeHPO}_4(\text{aq})$	$\text{Fe}^{+2} + \text{PO}_4^{-3} + \text{H}_2\text{O} = \text{FeHPO}_4(\text{aq}) + \text{OH}^-$	15.975 ^b
$\text{FeH}_2\text{PO}_4^+$	$\text{Fe}^{+2} + \text{PO}_4^{-3} + 2\text{H}_2\text{O} = \text{FeH}_2\text{PO}_4^+ + 2\text{OH}^-$	22.273 ^b
$\text{FeSO}_4(\text{aq})$	$\text{Fe}^{+2} + \text{SO}_4^{-2} = \text{FeSO}_4(\text{aq})$	2.39 ^b
KSO_4^-	$\text{K}^+ + \text{SO}_4^{-2} = \text{KSO}_4^-$	0.85 ^b
KHPO_4^-	$\text{K}^+ + \text{PO}_4^{-3} + \text{H}_2\text{O} = \text{KHPO}_4^- + \text{OH}^-$	13.255 ^b
MgOH^+	$\text{Mg}^{+2} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$	-11.397 ^b
$\text{MgCO}_3(\text{aq})$	$\text{Mg}^{+2} + \text{CO}_3^{-2} = \text{MgCO}_3(\text{aq})$	2.92 ^b
MgHCO_3^+	$\text{Mg}^{+2} + \text{CO}_3^{-2} + \text{H}_2\text{O} = \text{MgHCO}_3^+ + \text{OH}^-$	11.339 ^b
MgF^+	$\text{Mg}^{+2} + \text{F}^- = \text{MgF}^+$	2.05 ^b
MgPO_4^-	$\text{Mg}^{+2} + \text{PO}_4^{-3} = \text{MgPO}_4^-$	4.654 ^b

Table B-1. Aqueous Reactions Used in Geochemical Modeling ($T=25\text{ }^{\circ}\text{C}$, $I=0$).

Species	Reaction	log K
MgHPO ₄ (aq)	Mg ⁺² + PO ₄ ⁻³ + H ₂ O = MgHPO ₄ (aq) + OH ⁻	15.175 ^b
MgH ₂ PO ₄ ⁺	Mg ⁺² + PO ₄ ⁻³ + 2H ₂ O = MgH ₂ PO ₄ ⁺ + 2OH ⁻	21.256 ^b
MgSO ₄ (aq)	Mg ⁺² + SO ₄ ⁻² = MgSO ₄ (aq)	2.26 ^b
NaCO ₃ ⁻	Na ⁺ + CO ₃ ⁻² = NaCO ₃ ⁻	1.27 ^b
NaHCO ₃ (aq)	Na ⁺ + CO ₃ ⁻² + H ₂ O = NaHCO ₃ (aq) + OH ⁻	10.079 ^b
NaF (aq)	Na ⁺ + F ⁻ = NaF (aq)	-0.2 ^b
NaHPO ₄ ⁻	Na ⁺ + PO ₄ ⁻³ + H ₂ O = NaHPO ₄ ⁻ + OH ⁻	13.445 ^b
NaSO ₄ ⁻	Na ⁺ + SO ₄ ⁻² = NaSO ₄ ⁻	0.73 ^b
H ₂ SiO ₄ ⁻²	Si(OH) ₄ = H ₂ SiO ₄ ⁻² + 2H ⁺	-23.04 ^b
H ₃ SiO ₄ ⁻	Si(OH) ₄ = H ₃ SiO ₄ ⁻ + H ⁺	-9.84 ^b
SiF ₆ ⁻²	Si(OH) ₄ + 6F ⁻ + 4H ⁺ = SiF ₆ ⁻² + 4H ₂ O	30.18 ^b
HCO ₃ ⁻	CO ₃ ⁻² + H ⁺ = HCO ₃ ⁻	10.33 ^b
H ₂ CO ₃	CO ₃ ⁻² + 2H ⁺ = H ₂ CO ₃	16.68 ^b
HF (aq)	F ⁻ + H ⁺ = HF (aq)	3.17 ^b
HF ₂ ⁻	2F ⁻ + H ⁺ = HF ₂ ⁻	3.75 ^b
H ₂ F ₂ (aq)	2F ⁻ + 2H ⁺ = H ₂ F ₂ (aq)	6.768 ^b
HPO ₄ ⁻²	PO ₄ ⁻³ + H ⁺ = HPO ₄ ⁻²	12.375 ^b
H ₂ PO ₄ ⁻	PO ₄ ⁻³ + 2H ⁺ = H ₂ PO ₄ ⁻	19.573 ^b
H ₃ PO ₄	PO ₄ ⁻³ + 3H ⁺ = H ₃ PO ₄	21.721 ^b
HSO ₄ ⁻	SO ₄ ⁻² + H ⁺ = HSO ₄ ⁻	1.99 ^b

^a Allison et al., 1991

^b Schecher, 2001

^c Langmuir, 1997

^d Payne, 1999

^e Grenthe et al., 1992

^f Giammar, 2001

Table B-2. Solid Reactions Used in Geochemical Modeling (T=25 °C, I=0).

Species	Reaction	log K
Uranophane	$\text{Ca}^{+2} + 2\text{UO}_2^{+2} + 2\text{Si}(\text{OH})_4 = \text{Ca}(\text{UO}_2)_2[\text{SiO}_3(\text{OH})]_2 \cdot 5\text{H}_2\text{O} + 6\text{H}^+$	-17.49 ^b
UO ₂ (OH) ₂ (beta)	$\text{UO}_2^{+2} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-5.612 ^b
Rutherfordine	$\text{UO}_2^{+2} + \text{CO}_3^{-2} = \text{UO}_2\text{CO}_3$	14.5 ^b
Autunite	$\text{Ca}^{+2} + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$	44.7 ^a
H-Autunite	$2\text{H}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2$	48.42 ^a
K-Autunite	$2\text{K}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{K}_2(\text{UO}_2)_2(\text{PO}_4)_2$	48.244 ^b
Na-Autunite	$2\text{Na}^+ + 2\text{UO}_2^{+2} + 2\text{PO}_4^{-3} = \text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2$	47.6 ^a
UO ₂ (NO ₃) ₂	$\text{UO}_2^{+2} + 2\text{NO}_3^- = \text{UO}_2(\text{NO}_3)_2$	-12.148 ^b
UO ₂ (NO ₃) ₂ ·2H ₂ O	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 2\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	-4.851 ^b
UO ₂ (NO ₃) ₂ ·3H ₂ O	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 3\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	-3.39 ^b
UO ₂ (NO ₃) ₂ ·6H ₂ O	$\text{UO}_2^{+2} + 2\text{NO}_3^- + 6\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	-2.046 ^b
CaMg(CO ₃) ₂	$\text{Ca}^{+2} + \text{Mg}^{+2} + 2\text{CO}_3^{-2} = \text{CaMg}(\text{CO}_3)_2$	16.54 ^b
BIXBYITE	$2\text{Mn}^{+3} + 3\text{H}_2\text{O} = \text{Mn}_2\text{O}_3 + 6\text{H}^+$	0.644 ^b
BRUCITE	$\text{Mg}^{+2} + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + 2\text{H}^+$	-16.844 ^b
CALCITE	$\text{Ca}^{+2} + \text{CO}_3^{-2} = \text{CaCO}_3$	8.48 ^b
CHALCEDONY	$\text{Si}(\text{OH})_4 = \text{SiO}_2 + 2\text{H}_2\text{O}$	3.55 ^b
CRISTOBALITE	$\text{Si}(\text{OH})_4 = \text{SiO}_2 + 2\text{H}_2\text{O}$	3.35 ^b
DIASPORE	$\text{Al}^{+3} + 2\text{H}_2\text{O} = \text{AlOOH} + 3\text{H}^+$	-6.873 ^b
Fe(OH) ₂	$\text{Fe}^{+2} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + 2\text{H}^+$	-13.564 ^b
DOLOMITE (ord)	$\text{Ca}^{+2} + \text{Mg}^{+2} + 2\text{CO}_3^{-2} = \text{CaMg}(\text{CO}_3)_2$	17.09 ^b
FLUORITE	$\text{Ca}^{+2} + 2\text{F}^- = \text{CaF}_2$	10.5 ^b
Fe ₃ (PO ₄) ₂	$3\text{Fe}^{+2} + 2\text{PO}_4^{-3} = \text{Fe}_3(\text{PO}_4)_2$	36 ^b
Ca ₃ (PO ₄) ₂ (beta)	$3\text{Ca}^{+2} + 2\text{PO}_4^{-3} = \text{Ca}_3(\text{PO}_4)_2 \text{ (beta)}$	28.92 ^b
^a Allison et al., 1991		
^b Schecher, 2001		

PLATE 1

Lithologic Data

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Borehole 299-W19-43
Hanford Site - 200 West Area, UP-1 Operable Unit

HNF-45099 Rev. 0

C-1

PLATE 2

Sediment Mineralogy

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Primary Lithologic Symbols

- Sand (Very fine to coarse grained)
- Silty Sand
- Gravelly Sand/Sandy Gravel
- Silt/Clay
- Sandy Silt/Clay
- Calcareous Silty Sand
- Sand with Various Amounts of Carbonate Cement
- Calcareous Silt/Clay

- Notes and Legend:
- Temporary steel casing was advanced as the borehole was advanced. Twelve inch diameter casing was advanced to 50 feet; eight inch diameter casing was used to 295 feet. All casing was removed during well completion.
 - Cable tool drilling methods were used to advance the borehole. This included using a drive barrel (2.9" in length 7" I.D., 8" O.D. to 50 feet and a 1.85" drive barrel, 5" I.D., 7" O.D. to 272.5 feet). Hard tool drilling methods were used from 274.5 to total depth (295.72 feet). Split spoon sampling methods were used to recover in place soil samples; spoon dimensions 4" I.D., 5" O.D. and included 2 one foot Lexane liners.
 - All split spoon samples except one (25-27 foot interval) were collected for MSE-TA; split spoon sample from 25-27 feet was collected for Bechtel Hanford for waste designation. Sample recovery was 100%, except for MSE Core 124 (60% recovery).
 - Grab samples were collected by MSE in tin quart size cans as the borehole was advanced.

Legend

- Split spoon interval (2 feet)
- Water Table (257 feet)
- Erosional Unconformity
- DB Drive Barrel
- HEIS Hanford Environmental Information System
- BHI Bechtel Hanford Inc.
- WD Waste Designation
- CPT Cone Penetrometer Testing
- CPS Counts Per Second
- g/cm Grams Per Cubic Centimeter
- m³/g Meter Squared Per Gram
- ohm-m Ohm Meters
- pCi/g Pico Curie Per Gram

Scale 1" = 10'

DRAFT ONLY

Plate 2: Sediment Mineralogy

PLATE 3

Groundwater Geochemical Data

PLATE 4

Petrographic Analysis Data

Primary Lithologic Symbols

Notes and Legend:

1. Temporary steel casing was advanced as the borehole was advanced. Twelve inch diameter casing was advanced to 50 feet; eight inch diameter casing was used to 295 feet. All casing was removed during well completion.
2. Cable tool drilling methods were used to advance the borehole. This included using a drive barrel (2.9' in length 7" I.D., 8" O.D. to 50 feet and a 1.85" drive barrel, 6" I.D., 7" O.D. to 272.5 feet). Hard tool drilling methods were used from 274.5 to total depth (295.72 feet). Split spoon sampling methods were used to recover in place soil samples; spoon dimensions 4" I.D., 5" O.D. and included 2 one foot Lexane liners.
3. All split spoon samples except one (25-27 foot interval) were collected for MSE-TA; split spoon sample from 25-27 feet was collected for Bechtel Hanford for waste designation. Sample recovery was 100%, except for MSE Core 124 (80% recovery).
4. Grab samples were collected by MSE in tin quart size cans as the borehole was advanced.
5. Petrographic Analyses performed on standard thin-sections (grain mounts, 0.03mm) from core samples. Analyses is based on visual estimates and point-count data.
6. Amount of Matrix/Cement and especially porosity often unable to be determined from grain mounts of coarser grained material. Typically, framework, matrix, cement and porosity equals the whole rock (100 percent). The total framework was classified into quartz, feldspar, rock fragments (100 percent).
7. Fraction of total framework (percent) with alterations and coatings; one hundred percent indicates that all framework is coated or enveloped by matrix/cement and no observable porosity.
8. Framework with alterations and coatings include Goethite-Limonite (G-L), Hematite (H), Clay (C), Carbonate (C) and Magnetite-Ilmenite (M-I). Each is shown as a percent of the total.
9. Magnetite-ilmenite (M-I) chiefly occurs in basaltic rock fragments as primary mineralogy.

Scale 1" = 10'

(257)

C-4

ATTACHMENT
Lawrence Berkley Uranium Analyses

This EXCEL table was obtained in January 2010 from Lawrence Berkley National Laboratories (LBL) by Jeff Serne of Pacific Northwest National Laboratory (PNNL). The work was done under a 2001-2004 MSE contract through MSE and PNNL. This contract was funded by DOE Headquarters. The LBL scope of work was to measure the presence of uranium isotopes, including uranium 236, in soil samples for boreholes adjacent to Hanford waste site 216-U-1&2. This data was supposed to be included in the original report, but the data failed to get to MSE or PNNL until 2010.

These results were supposed to be included in the MSE, 2004 report, *Development of a Geochemical Model for Uranium Transport in the Unsaturated and Saturated Sediments at the 200 West Area of the U.S. Department of Energy Hanford Site, Washington* (MSE/ECCP-41; September, 2004).

Scot C. Adams

February, 2010

Adams, Scot C

From: Serne, R Jeffrey [jeff.serne@pnl.gov]
Sent: Thursday, January 28, 2010 6:57 PM
To: 'John Neil Christensen'
Subject: RE: RE: U-236 Measurements for MSE
Attachments: U-1 U-2 Cribs 200 West.xls

Great! No need to get Cricket graph. It appears to me that you definitely found enough U-236 in all but the two samples that must be 299-W19-14 at 185 and 190 ft to say there is waste present in the W19-15, W-19-16 and W19-17 samples analyzed. You appear to have run 9 of the 20 sediments on the Table 5-1 list (which also included a White Bluffs caliche sample from across the river. I highlighted ones that seem to offer no question on presence of reprocessed fuel U. Do you agree?

I will also look at the ratios of U-234 and U-235 vs all our 200 E data just out of curiosity. Some of the depths might be in CCUz similar to Kate Maher's samples but with contamination excepting maybe W19-14. I will figure out what strata they reside in to see if we could add them Kate's data set for CCUz if you think they are low enough on the U-236.

Did MSE send you water extracts or aliquots of sediment that you processed yourself? Would it have made a difference if they sent acid extracts? Do you recall if you had pre-knowledge on total U or did you measure total U yourself?

How is the B Complex thinking and 3 samples coming???

R. Jeff Serne
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-----Original Message-----

From: John Neil Christensen [mailto:JNChristensen@lbl.gov]
Sent: Thursday, January 28, 2010 6:36 PM
To: Serne, R Jeffrey
Cc: 'Donald DePaolo'
Subject: Re: RE: U-236 Measurements for MSE

Jeff,

If I remember correctly, those were samples from around the U-1,2 cribs in the 200 West area. I did analyze archived samples from various cores, and I remember distinctly sending along that U isotopic data to who ever wanted it way back when. I managed dig that data up again, see attached excel file (the original file was created July, 2004, so I suppose that was when I sent it along. I also found an old Cricket Graph file I, alas, can no longer open). If they want, I can look at the data again and provide my take (re-take) again.

John

John N. Christensen
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Berkeley, CA 94720
(510) 486-6735

Sample	Depth interval	Mean depth, feet	234U/238U	error $\pm 2s$	238U/235U	error $\pm 2s$	236U/238U	error $\pm 2s$
15A	160' to 165'	162.5	54.34	0.09	145.691	0.078	61.07	0.09
			54.32	0.07	145.598	0.046		
		wted ave	54.328	0.055	145.621	0.039		
15B	165' to 166'	165.5	55.23	0.09	143.751	0.077	47.47	0.10
			55.37	0.08	143.816	0.045		
		wted ave	55.31	0.06	143.800	0.039		
15C	167' to 170'	168.5	54.69	0.12	145.073	0.073	57.26	0.12
16A	160' to 165'	162.5	53.8	0.07	148.602	0.048	110.77	0.16
			53.72	0.07	148.659	0.048		
		wted ave	53.76	0.049	148.630	0.034		
16B	167' to 170'	168.5	54.02	0.09	148.144	0.081	107.27	0.16
17A	160' to 165'	162.5	54.53	0.08	147.303	0.043	127.19	0.16
			54.57	0.08	147.183	0.043		
		wted ave	54.55	0.055	147.183	0.043		
17B	165' to 170'	168.5	54.65	0.08	147.228	0.042	127.66	0.16
			54.56	0.08	147.310	0.054		
			54.605	0.057	147.259	0.033		
14A	185'	185	55.53	0.008	137.89	0.1	0.681	0.001
14B	190'	190 need repeat?	55.84	0.008	139.02	0.102	2.268	0.04

U-1 U-2 cribs 200 West.xls

Adams, Scot C

From: Serne, R Jeffrey [jeff.serne@pnl.gov]
Sent: Friday, January 29, 2010 7:49 AM
To: Adams, Scot C; Truex, Michael J; Um, Wooyong
Subject: FW: RE: RE: U-236 Measurements for MSE
Attachments: 200 West cores prelim.pdf

Here is more info on the MSE-LBNL connection. It looks like the U isotope signatures from each borehole represent a different fuel source and thus likely different disposal source. By different disposal source I do not necessarily mean different crib but at least different disposal campaign into a crib. As I suspected from the spreadsheet ratios sent last night the two data points from well W19-14 appear to be uncontaminated natural U of only very faintly contaminated.

What we really need are U total concentrations now that we have confirmed that there is some level of contamination in many of the sediments. But be cognizant that the isotopic ratio data generated by LBNL-UCB are incredibly sensitive--that is they can measure a "speck" of Hanford U in a "ton" of natural U already present in the sediment from creation. So we need absolute concentrations to decide whether we have useful sediment in core library.

R. Jeff Serne
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-----Original Message-----

From: John Neil Christensen [mailto:JNChristensen@lbl.gov]
Sent: Thursday, January 28, 2010 7:12 PM
To: Serne, R Jeffrey
Subject: Re: RE: RE: U-236 Measurements for MSE

Jeff,

And here's a pdf I made at the time (you can tell because I was still plotting 238U/235U, now I'm reformed and now use 235U/238U).

I don't rightly remember what I got. I suspect it was extracts of some sort (I found a file with some data that probably came from you? titled "Info on MSE U-Isotope Work"). Anyway, I think I analyzed all the samples that I had gotten. I bet I had pre-knowledge (hence the file). I think there may be some data on caliche samples that Mike Singleton collected (that will require some more digging). That might be of interest for the report.

I'm working on those three samples right now. So far it looks like the CCZ fits, but I haven't reduced it yet.

John

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----- Original Message -----

From: "Serne, R Jeffrey" <jeff.serne@pnl.gov>
Date: Thursday, January 28, 2010 6:57 pm
Subject: RE: RE: U-236 Measurements for MSE
To: 'John Neil Christensen' <JNChristensen@lbl.gov>

> Great! No need to get Cricket graph. It appears to me that you
> definitely found enough U-236 in all but the two samples that must be
> 299-W19-14 at 185 and 190 ft to say there is waste present in the
> W19-15, W-19-16 and W19-17 samples analyzed. You appear to have run 9
> of the 20 sediments on the Table 5-1 list (which also included a White
> Bluffs caliche sample from across the river. I highlighted ones that
> seem to offer no question on presence of reprocessed fuel U. Do you
> agree?
>
> I will also look at the ratios of U-234 and U-235 vs all our 200 E
> data just out of curiosity. Some of the depths might be in CCUz
> similar to Kate Maher's samples but with contamination excepting maybe
> W19-14. I will figure out what strata they reside in to see if we
> could add them Kate's data set for CCUz if you think they are low
> enough on the U-236.
>
> Did MSE send you water extracts or aliquots of sediment that you
> processed yourself? Would it have made a difference if they sent
> acid extracts? Do you recall if you had pre-knowledge on total U or
> did you measure total U yourself?
>
> How is the B Complex thinking and 3 samples coming???

> R. Jeff Serne
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> Tel: 360-539-6162
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> -----Original Message-----

> From: John Neil Christensen [mailto:JNChristensen@lbl.gov]
> Sent: Thursday, January 28, 2010 6:36 PM
> To: Serne, R Jeffrey
> Cc: 'Donald DePaolo'
> Subject: Re: RE: U-236 Measurements for MSE

>
 > Jeff,
 >
 > If I remember correctly, those were samples from around the U-1,2
 > cribs in the 200 West area. I did analyze archived samples from
 > various cores, and I remember distinctly sending along that U isotopic
 > data to who ever wanted it way back when. I managed dig that data up
 > again, see attached excel file (the original file was created July,
 > 2004, so I suppose that was when I sent it along. I also found an old
 > Cricket Graph file I, alas, can no longer open).
 > If they want, I can look at the data again and provide my take (re-
 > take) again.
 >
 > John
 >
 >
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Isotopic Composition of Uranium from DI H₂O Rinses of Archived Sediment Cores in the Vicinity of the U-1, U-2 Cribs, 200 West

200 West Cores prelim. pdf