Phase I Nuclide Partition Laboratory Study Influence of Cellulose Degradation Products on the Transport of Nuclides from SRS Shallow Land Burial

by

S. M. Serkiz

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

D. Knaub

H. Uhal

DOE Contract No. **DE-AC09-96SR18500**

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

WSRC-TR-98-00460
Revision 0

Keywords: Radionuclide Speciation
and Transport, Cellulose
Degradation, Dissolved Organic
Matter, Europium, Uranium, E-Area
Vaults, Performance Assessment

Retention: Permanent

**Phase I Nuclide Partition Laboratory Study
Influence of Cellulose Degradation Products
On the Transport of Nuclides from
SRS Shallow Land Burial Facilities (U)**

December 20, 1998

S. M. Serkiz, Waste Processing Technology
SRTC, Building 773A

D. Knaub and H. Uhal,
Environmental Systems Engineering Dept.
Clemson University

Authorized Derivative Classifier

Savannah River Technology Center
Westinghouse Savannah River Company
Aiken, SC 29808

Author

Steven M. Serkiz 12/20/98
S. M. Serkiz, Waste Disposal & Environmental Development Date

Design Check

Daniel I. Kaplan 12/21/98
D. I. Kaplan, Waste Processing Technology Date
(per Manual E7, Procedure 2.40)

Approvals

B. T. Butcher 1/3/99
B. T. Butcher, Level 4 Manager Date
Waste Disposal & Environmental Development - SRTC

1.0 Executive Summary

Degradation products of cellulosic materials (e.g., paper and wood products) can significantly influence the subsurface transport of metals and radionuclides. Codisposal of radionuclides with cellulosic materials, for example in the E-Area slit trenches at the SRS, is therefore, expected to influence nuclide fate and transport in the subsurface. In a previous modeling activity, significant differences in the radionuclide inventory of the E Area slit trench were determined when the presence of CDP was accounted for in the conceptual model. For example, the inventory of U-233 and Pu-240 were calculated to be 26% and 48% lower, respectively, when CDP was present.

Due to the complexities of these systems and the paucity of site-specific data, the effects of cellulose waste loading and its subsequent influence on nuclide transport are not well established. A series of studies were initiated in April 1998 to validate and/or update the modeling assumptions and results. Phase I, the subject of this report, employed a surrogate organic matter (OM) source to represent the influence of (CDP) on nuclide sorption to General Separation Area (GSA) soils. In particular, the sorption of the trivalent lanthanide Eu^{3+} and the divalent actinide UO_2^{2+} to SRS soils or clays prevalent at SRS in the presence of this CDP surrogate was examined in a series of laboratory experiments.

The results of these studies clearly demonstrate that both pH and organic matter have a significant influence on europium and uranium mobility in SRS shallow waste burial environments. Furthermore, these variables are highly interrelated.

Even in the absence of organic matter the sorption of uranyl and Eu (III) is nonlinear with respect to pH. With small changes in pH values in some regions causing very large changes in sorption and K_d values. Cellulose will degrade to form natural organic acids and these materials are capable of reducing the pH of the system. This pH reduction can, in turn, significantly affect the metal sorption behavior simply by altering the pH of the system. Therefore, the current concentration K_d approach, which does not take into consideration pH and the effect of organic complexes, may not be adequate in systems containing CDP.

These experiments show that sorption of natural organic matter varies as a function of pH and total carbon content. Organic matter sorption increases with decreasing organic carbon content and decreasing pH. Over the range of experimental conditions examined in this study sorption of organic matter to soil minerals varied from several percent to about 60 percent. These effects are systematic and should be accounted for in future modeling phases of this work.

In the presence of naturally occurring organic matter a significant effect of pH and organic matter concentration was observed for U and Eu sorption. Over the range of experimental conditions examined in this study the following summarizes the influence of CDM surrogate on U and Eu sorption (i.e., decreased mobility):

	<u>Low Organic</u>	<u>High Organic</u>
<u>Low pH</u>	↑ sorption	↑ sorption
<u>High pH</u>	no effect	↓ sorption

For a particular pH value, the influence of CDP on the sorption of the nuclide of interest varied from no change to almost 100 percent change. Based on Phase I results, codisposal of cellulosic materials is expected to have a significant effect on nuclide mobility in and around the E-Area Slit Trenches. Due to the complexities of this system further work will be completed in the subsequent phases of this project. During Phase II, these findings will be further elucidated through studies using actual CDP and complex natural sediments.

2.0 Introduction

Cellulosic materials (e.g., wood and paper products) readily degrade in the environment to form cellulose degradation products (CDP) in both the solid and dissolved (i.e., dissolved organic matter (DOM)) phases. The effects of organic matter (OM) on the speciation (i.e., chemical form) and mobility of nonradioactive elements (Perdue and Gjessing, 1990; Thurman, 1985; and Stumm and Morgan, 1981) and radioactive elements (Choppin 1988; Allard et al. 1989; Fairhurst et al. 1995; and Ledin et al. 1994) are well documented in the open literature. Codisposal of radionuclides with cellulosic materials is, therefore, expected to influence nuclide fate and transport in subsurface. The disposal and degradation of wood products in the E-Area slit trenches at the SRS are a source of OM that is expected to influence radionuclide fate.

Insights into the fate of cellulosic material in SRS burial trenches can be drawn from the extensively studied behavior of naturally occurring organic matter in forested ecosystems. In both of these environments cellulosic materials are expected to decay to form a complex mixture of natural organic acids (e.g., humic and fulvic acids). These organic acids in forested ecosystems make up the majority of naturally occurring soil and dissolved organic matter (Thurman, 1985). Even though this OM will ultimately degrade to CO₂ or methane, steady state dissolved organic carbon concentrations in soil porewater resulting from

tree and leaf litter decay processes can be as high as several hundred mg C/L (Thurman, 1985). As an example, a typical soil profile is shown in Figure 1.

The complexities of the OM cycle are illustrated in Figure 1. With the major processes that influence organic matter fate and transport in near surface systems including (1) DOM production from cellulose degradation and leaching, (2) metal/nuclide complexation with DOM, (3) sorption of organic matter to soil surfaces, and (4) mineralization of organic matter by soil microbes. Some of these processes act to enhance metal/nuclide transport while others act to inhibit their transport. In the SRS slit trenches the dominant processes are not known. Modeling results (Serkiz and Myers, 1996), however, suggest that the dissolved fraction of these CDP will form complexes with radionuclides, reducing radionuclide sorption to soil surfaces, and, thereby, increasing their mobility.

2.1 Previous Performance Assessment Modeling of CDP

A modeling exercise (Serkiz and Myers, 1996) was undertaken to estimate the influences of the codisposal of wood products on the inventory limits of various radionuclides in the E-Area slit trenches. This modeling effort consisted of coupling several well established geochemical and groundwater flow models to estimate the effects of organic matter on the mobility of radionuclides in groundwater migrating from the source area.

The Radiological Performance Assessment for the E-Area disposal facility included inventory limits for 29 elements (56 isotopes). Of these 29 elements, Am, Bk, Cf, Cm, Cs, Ni, Np, Pd, Pu, Rb, Sr, U, and Zr had a groundwater-limiting pathway and have been shown to interact with naturally occurring OM (MMES, 1994). The effects of cellulose degradation products on the fate and transport of isotopes of these 13 elements were evaluated in the modeling exercise.

Due to the complexities of these systems and the paucity of site-specific data, the effects of cellulose waste loading and its subsequent influence on nuclide transport are not well established. Therefore, Serkiz and Myers (1996) made a number of assumptions to complete this modeling exercise. These assumptions included:

- citric acid or ethylenedinitrilotetraacetic acid (EDTA) are adequate surrogates for the nuclide complexation chemistry of the mixture of organic compounds that comprise cellulose degradation products;
- a linear sorption isotherm (i.e., a K_d) approach, as used in the performance assessment modeling (MMES, 1994), is adequate to describe nuclide partitioning to soil surfaces as a function of changing trench geochemical conditions; and

- aqueous organic matter concentration derived from cellulose degradation was 30 mg C/L and exhibits no temporal variations.

Using this modeling approach, OM generated from cellulose degradation was predicted to have no effect on the inventory limits for Cs, Np, Rb and Zr. The inventory limits for the isotopes of Am, Cf, Cm, Bk, Ni, Pd, Pu, Sr, and U calculated in the presence of this OM were predicted to decrease over a range of 26% for U-233 to 48% for Pu-240 from previous model predictions. The details of this modeling effort are documented in Serkiz and Myers (1996). These calculations provided important first approximations of radionuclide mobility in various scenarios, however, the underlying assumptions require validation. Additionally, it is necessary to determine whether these assumptions are in fact conservative (i.e., provide an overestimate of radio-isotope transport).

2.2 Validation Studies

To investigate major processes that influence nuclide transport in the presence of CDP, the effects of CDP character, CDP fate, and nuclide partitioning in the presence of CDP were investigated. More specifically, four research areas will be investigated during each study phase as follows:

1. Characterization of CDP.
 - a. Phase I – development of CDP organic surrogate from existing data.
 - b. Phase II – cellulose leaching study to collect data on the rate of formation and character of degradation products.
 - c. Phase III – validate or update current model with laboratory data.
2. CDP Fate.
 - a. Phase I – sorption of CDP organic surrogate to SRS soils and SRS reactive mineral surfaces.
 - b. Phase II –
 - (1) sorption of CDP to SRS soils,
 - (2) collect cellulose degradation rate data.
 - c. Phase III – validate or update current model with laboratory data.
3. Radionuclide Partitioning Studies
 - a. Phase I – CDP Surrogate Study
 - (1) pH effects (3 to 10),
 - (2) effect of CDP surrogate concentration (0, 10, 30, and 500 mgC/L),
 - (3) nuclide valence effect (UO_2^{2+} and Eu^{3+}).
 - b. Phase II – Laboratory Generated CDP Study
 - (1) pH effects (3 to 10),
 - (2) effect of CDP concentration.
 - c. Phase III – validate or update current model with laboratory data.

4. Model Validation/Trench Limit Update
 - a. Phase I – comparison of CDP organic surrogate data with current model assumptions.
 - b. Phase II – comparison of CDP data with surrogate data and current model assumptions.
 - c. Phase III – validate or update current model and, if necessary, recalculate trench limits.

3.0 Organization

The remainder of this report is organized around the four areas described above (Characterization of CDP, CDP Fate, Radionuclide Partitioning Studies, and Model Validation/Trench Limit Update). Because the Characterization of CDP is a literature review activity in Phase I, it will be presented as a discussion separate from the laboratory studies in Section 4 of this report. Sections 5 and 6 consist of the methods description and results discussion, respectively, for the Phase I CDP Fate and Radionuclide Partitioning Studies. Conclusions and summary are presented in Section 8.

4.0 Phase I - Characterization of CDP

Cellulose degradation produces a complex mixture of compounds as shown by Serne et al. (1993). These researchers characterized CDP in leachate from paper and wood after twelve weeks of aging and were able to identify less than 4% of the total organic carbon as specific organic compounds. Furthermore, it has been shown that leaf litter (a cellulose based source material) leachate varies in character and quantity as a function of aging time, temperature, and moisture content (Serkiz, 1991). We, therefore, also expect that CDP exported from SRS disposal trenches would exhibit temporal variations in quality and quantity.

The complexities of these systems and the paucity of site-specific data have necessitated the use of chemical surrogates to represent the CDP chemistry in performance assessment modeling. This is, in large part, due to the lack of physicochemical constants for nuclide-CDP complexes, CDP sorption to soil surface, and rate of CDP degradation.

4.1 Current Modeling Approach

Because of the lack of site-specific data and difficulties in modeling the chemical composition of CDP (a complex mixture of compounds), it was necessary to simplify the representation of CDP through use of surrogate organic compounds in the modeling effort. It was assumed that cellulose materials degrade to constantly produce DOM at 30 mg C/L. A source concentration of 79 mg/L citrate (30 mg C/L) was selected based on dissolved organic matter production

from a simulated waste-form containing approximately 40% wood products (Serne et al., 1993). This DOM was then available to react with other components in the model system (e.g., major ions, nuclides, and soil surfaces).

Citrate was selected as a surrogate for OM because it is a hydroxy-carboxylic acid typical of cellulose degradation products (Baston et al., 1992) and stability constants for reaction complexes between citrate and numerous radionuclides are available in the open literature. Additionally, citrate is expected to exhibit behavior similar to acetic acid, a major product in the anaerobic degradation of creosote (Cozzarelli et al., 1994). Therefore, citrate is believed to be a reasonable analogue for cellulose degradation products.

Due to the lack of stability constants for reactions between citrate and Pd, PuO₂, and Zr, ethylenedinitrilotetraacetic acid (EDTA) was used as a surrogate with these elements. EDTA was selected because stability constants for reaction complexes between EDTA and numerous radionuclides are available in open literature and it is a strong complexing agent and should, therefore, act as a conservative surrogate for CDP. A source concentration of 69 mg/L EDTA (30 mg C/L) was used.

4.2 Selection of CDP Surrogate for Phase I Laboratory Studies

As a result of the sorption and decay processes discussed above, a significant amount of the organic carbon remaining in solution is transformed into large molecules that contain aromatic rings, aliphatic chains, and carboxylic and phenolic functional groups (see Figure 2). This naturally occurring dissolved organic matter, like CDP, is a complex mixture of organic compounds that is dominated, on a molar basis, by oxygen containing functional groups.

DOM, like CDP, is a complex mixture of organic compounds. Furthermore, cellulose degradation processes in forested ecosystems are believed to be a reasonable analogue for cellulose degradation in SRS waste trenches. Therefore, naturally occurring DOM is expected to be more representative of CDP than simple organic acids like citrate or EDTA used in the initial modeling study. A well-characterized DOM sample isolated from the Suwannee River was chosen as a surrogate for CDP in the Phase I laboratory studies.

As a means to validate data generated on surrogate compounds, these data will be compared with confirmatory experiments conducted with actual CDP generated in Phase II of this study. If there are significant discrepancies between surrogate and CDP studies, other methodologies (e.g., use of conditional stability constants) will be evaluated.

5.0 Phase I – Materials and Methods for CDP Fate and Radionuclide Partitioning Studies

Adding to the complexity of describing nuclide transport in the presence of CDP, is the mixture of reactive surfaces that comprise SRS soils. These reactive sorption surfaces include kaolinite, hydrous ferric oxide (HFO), and, in the case of this analysis, sorbed organic matter. Even though the majority, by weight or volume, of near-surface SRS soils is comprised of sand, the total surface area is derived primarily from the clay content of the soil (Johnson, 1995). Mineralogical analyses of samples collected in the vicinity of the F and H Seepage Basins of the General Separations Area (GSA) (Johnson, 1994) and other site-wide studies (Strom and Kaback, 1992) show that kaolinite is the major clay mineral in near surface sediments at SRS. Furthermore, Johnson (1995) and Findley (1998) showed that extractable iron and aluminum were ubiquitous in both GSA and site background soils. These extractable iron and aluminum minerals are represented by amorphous iron oxide (i.e., hydrous ferric oxide (HFO)) in our conceptual soil particle (see Figure 3).

In a further attempt to simplify the sorption surface in Phase I experiments, one set of experiments examined sorption of uranium (VI) to kaolinite in the presence and absence of Suwannee River dissolved organic matter. The other set of experiments investigated the sorption of europium (III) to a whole soil sample collected from the GSA also in the presence and absence of Suwannee River DOM. The approach of using lanthanides or rare earth elements as chemical surrogates for the trivalent actinides (Pu^{3+} , Am^{3+} , and Cm^{3+}) is well established (Choppin, 1989; Krauskopf, 1986). In addition to being able to investigate differences between whole soil and single mineral phase behavior in these systems, this approach should provide insight into the influence of the contaminant ion valence (UO_2^{2+} and Eu^{3+}) on nuclide behavior in these systems. Because of the inherent differences in these two studies described above, they will be addressed separately in the remainder of this report.

5.1 Materials and Methods – Kaolinite/Uranyl/DOM System

5.1.1 Materials

All solutions were prepared from reagent grade chemicals using DI water in acid-washed, double rinsed glassware, unless otherwise specified. Sorption experiments were completed using low-carbonate water prepared by boiling DI water followed by cooling in air stripped of carbonate by aeration through a 1 mol/L NaOH. Hydrogen ion activity (i.e., pH) was adjusted with standardized NaOH prepared from a saturated solution; HNO₃ served as the standardized acid.

Kaolinite

An Aiken kaolinite clay was obtained from the W R Grace & Co. of Aiken, SC, and is typical of material found on the Savannah River Site. The specific surface area of untreated Aiken kaolinite was $21.92 \pm 0.13 \text{ m}^2 \text{ g}^{-1}$ (Johnson, 1995).

A stock suspension of this kaolinite in the size range 0.2 μm to 2 μm was prepared using the method of Mattigod, *et al.* (1985). This pretreatment procedure removes oxide and hydroxide coatings from, but does not adversely affect, kaolinite surfaces. DI water suspensions of kaolinite clay (~75 g/L) were adjusted to pH 9.5 with 0.1 M NaOH and divided into 250-ml Nalgene bottles. The capped bottles were placed in a shaker bath at 25° C at 125 rpm overnight to allow the suspensions to equilibrate. The <2 μm fraction was separated by centrifuging at 1000 rpm for 2.8 minutes. The supernate was decanted and saved. The sediment was resuspended in DI water and recentrifuged at 1000 rpm for 2.8 minutes. The supernate from this centrifugation was decanted and saved, while the sediment was discarded. All supernate (approximately 2 L) was placed in 250 ml Nalgene bottles. The >0.2 μm fraction was separated by repeated centrifugation at 4000 rpm for 18 minutes, followed by discarding of the supernate and resuspension of the sediment in DI water. The residual clay (0.2 to 2 μm fraction) was then suspended in 0.2 M NaClO₄ adjusted to pH 3 with perchloric acid. The clay was repeatedly centrifuged and resuspended in the acidified NaClO₄ until a pH of about 3 was sustained. The clay was then further centrifuged, decanted, and resuspended in 0.1 M NaClO₄ at pH of 5.5. The prepared stock kaolinite suspension (66 g/L) was refrigerated at 4° C in a capped 1-L Nalgene bottle for subsequent adsorption experiments.

Organic Matter

The isolated organic matter (OM) used in this study was collected from the Suwannee River and has been extensively characterized (Serkiz and Perdue, 1991). This natural OM is a complex mixture of organic compounds, and is

believed to resemble more closely the products from the degradation of cellulosic material than any single organic compound.

Suwannee River DOM is a complex mixture of humic substances (fulvic acid and humic acid), hydrophilic acid, and simple compounds (carbohydrates, carboxylic acids, amino acids, and hydrocarbons). Humic and fulvic substances account for 24 and 37 percent respectively of the dissolved organic carbon present in the DOM used in this study (Serkiz and Perdue, 1991).

A stock solution of DOM at a final concentration of approximately 1300 mg C/L was prepared by dissolving 269.05 mg of lyophilized Suwannee River DOM isolate described above (Lot No. 45) in 100 ml of DI water.

Uranyl Solution

A 10^{-6} M uranyl solution was prepared from a depleted uranyl nitrate salt. The purity of this solution was checked by ion coupled mass spectrometry (ICP-MS). The chemical form of uranium, as uranyl ion, was inferred from redox measurement of experimental solutions made before and after equilibration.

5.1.2 Sorption of DOM on kaolinite

The first part of the experiment followed the approach of investigating DOM sorption on kaolinite presented in Murphy, *et al.* (1990). This was intended to serve as a baseline for the uranyl sorption experiments outlined below.

A kaolinite working suspension was prepared by mixing 60 ml of the kaolinite stock suspension and 0.1 M NaClO_4 to a total volume of 1 L. The working suspension was adjusted to a pH of 8.0 with 0.1 N NaOH and placed on an unheated shaker table at 125-rpm overnight to equilibrate. Ambient temperature for this and subsequent experiments was 25° C.

Twelve 42-ml Oak Ridge centrifuge tubes were filled with samples and blanks, as specified by the matrix shown in Table 1. The pH of the working suspension was adjusted by incrementally adding 0.1 N NaOH to reach the target pH prior to filling each tube. All tubes were placed on a shaker table under ambient temperature conditions and shaken at 150 rpm overnight (>19 hours) to equilibrate.

The tubes were then centrifuged at 10,000 rpm for 20 minutes. A portion (30ml) of the supernate from each tube was filtered through a 0.45- μm Acrodisc single-use filter into a 30-ml Nalgene bottle. The filtered samples were refrigerated at 4° C and later analyzed for TOC. Following pH measurement of each tube, the kaolinite was resuspended in the remaining supernate. The resulting kaolinite

suspensions from samples 81-1, and 81-3 to 81-11 were transferred to 15-ml glass vials for oven drying at 65° C. Following drying and weighing the DOM/kaolinite sediments were saved for later TOC analysis.

5.1.2 Uranyl sorption kinetics in DOM and kaolinite system

A second experiment was performed to evaluate the kinetics of uranyl sorption in the DOM-kaolinite system and to determine an equilibrium sorption time for use in later experiments.

A kaolinite working suspension was prepared by mixing 63 ml of the kaolinite stock in 0.1 M NaClO₄ to a total volume of 1 L. The resulting suspension was allowed to equilibrate overnight on an unheated shaker table at 150 rpm.

23.9 ml of DOM stock solution was added to 999 ml of the kaolinite working solution to yield a final carbon concentration of 30.1 mg/L. The composite mixture was placed on an unheated shaker table at 150 rpm for 30 minutes to equilibrate, then divided into two equal batches (A and B). The pH of batch A was lowered to a target value of 3 by adding 0.2 N HClO₄, while the pH of batch B was raised to a target value of 8 by adding 0.1 N NaOH. The two batches were placed on an unheated shaker table at 200 rpm over the weekend to equilibrate. Final pH was 3.04 and 7.25, respectively.

Sixteen 42-ml Oak Ridge centrifuge tubes were filled with samples and blanks, as specified by the matrix in Table 2. Batch B tubes (pH 7) were filled in a glove bag purged with air bubbled through a CO₂ scrubber.

After filling, all tubes were placed simultaneously on an unheated shaker table at 250 rpm. Tubes were removed from the shaker table at the target times and immediately centrifuged at 10,000 rpm for 15 minutes. A portion (30ml) of the supernate from each tube was filtered through a 0.45-μm Acrodisc single-use filter into a 30-ml Nalgene bottle and its pH was measured. The filtered samples were refrigerated at 4° C for later ICP-MS analysis. The remainder of the supernate from each tube was discarded, and the sediment was resuspended in 10 ml of DI water, then transferred to pre-weighed 15-ml glass vials for oven drying at 65° C. Following weighing the sediments were saved for later TOC analysis.

5.1.3 Uranyl sorption in DOM and kaolinite system

A third experiment was performed to measure the sorption of uranyl ions in the DOM-kaolinite system. The equilibration time used was 19.75 hours, a duration that is in excess of the maximum time required to reach equilibrium conditions as determined from the sorption kinetics experiment.

A kaolinite working suspension was prepared by mixing 68 ml of the kaolinite stock suspension in 0.1 M NaClO₄ (prepared from low CO₂ DI water) to a total volume of 1 L. The resulting suspension was allowed to equilibrate for 4 hours on an unheated shaker table at 125 rpm.

23.9 ml of DOM stock solution was added to the kaolinite working solution to yield a final carbon concentration of 30.1 mg/L. The pH was adjusted to a target value of 7 by addition of 0.1 N NaOH. The solution was placed on an unheated shaker table at 150 rpm to equilibrate. Final pH was 7.12.

Twenty-six 42-ml Oak Ridge centrifuge tubes were filled with samples and blanks, as specified by the matrix in Table 3. This represents duplicate runs of 13 separate experimental conditions. The pH was adjusted by incrementally adding 0.1 N NaOH or 0.2 N HClO₄ to the working suspension to reach target pH prior to filling each tube. All transfers were performed in a glove bag purged with air bubbled through a CO₂ scrubber. All tubes then were placed on an unheated shaker table at 150 rpm for 19.75 hours to equilibrate.

Tubes were removed from the shaker table and centrifuged at 10,000 rpm for 15 minutes. A portion (30ml) of the supernate from each tube was filtered through a 0.45-μm Acrodisc single-use filter into a 30-ml Nalgene bottle after measuring its pH. The filtered samples were refrigerated at 4° C for later ICP-MS analysis.

The remainder of the supernate from each tube was discarded, and the sediment was resuspended in 10 ml of DI water, then transferred to tared 15-ml glass vials for oven drying at 65° C. Following drying and weighing the sediments were saved for later analysis.

5.1.3 Analytical Measurements

Oxidation-Reduction Potential

To ensure uranyl ions were not being reduced during the experiments, oxidation-reduction potential of the solutions was measured using a platinum electrode before addition of uranium and after equilibration and the results compared (see Table 4).

Uranium Analysis

A Fison Instruments inductively coupled plasma (argon) mass spectrometer (ICP-MS), modified VG PlasmaQuad PQ1 was used to determine uranium concentrations.

pH

All pH measurements were made using a Fisher Accumet pH meter, model 50, equipped with a glass electrode, Ross model 8103. The pH meter was calibrated daily using standard buffer solutions (Fisher Scientific).

Total Organic Carbon

Samples were analyzed for total carbon (TC) using a Shimadzu TOC-2000 total organic carbon analyzer with solid sample module.

5.2 Materials and Methods – SRS Whole Soil/Europium System

5.2.1 Materials

All solutions were prepared from reagent grade chemicals using DI water in acid-washed, double rinsed glassware, unless otherwise specified.

SRS Soil

The soil used for this study, identified as GC5, was collected from a location in the F Area of SRS known as the "Little Grand Canyon." Lithologically, this sample is identical to the surface soils in the Burial Ground Complex. Previous sorption studies of uranyl and cadmium have been conducted on this sample and, as part of these studies, the soil was well characterized by Johnson (1995) and Johnson (1994). Soil texture was characterized as 96.1% sand, 0.0% silt, and 3.8 % clay. The dominant minerals in the clay-size fraction were kaolinite and to a lesser extent, illite. The measured cation exchange capacity (CEC) was 3.9 meq/kg and the soil pH in water was 4.78. Although carbon content of this particular sample was not measured, all other samples they collected had a carbon content of less than 0.05%. It was assumed that the carbon content of this sample is below the analytical detection limit, but will be verified. Details of the soil characterization can be found in Johnson (1994) and Johnson (1995).

Solution Chemistry

To simulate leaching of contaminants from the disposal area, synthetic rainwater was chosen as the major ion chemistry in contact with the soil. The synthetic rainwater was prepared by the method of Lee and Weber (1979) (0.6414mg/L NH_4Cl , 0.7486 mg/L CaSO_4 , 0.4251mg/L NaNO_3 , 0.2022 mg/L KNO_3 , 0.7151mg/L $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). After equilibration with the atmosphere, the resulting solution pH was 5.20.

Organic Matter

The organic matter (OM) that was used was collected from the Suwannee River and has been extensively characterized (Serkiz and Perdue, 1991) and is the same material described above in the kaolinite/uranium/DOM experiments.

Europium Solution

A 10,000 ppm Eu^{3+} standard in 5% HNO_3 was obtained from Spex Centriprep (lot # HS-94Eu). A stock solution in 1% HNO_3 was prepared at a concentration of 10 ppm Eu, which was used to spike each sample. From this stock, calibration standards also in 1% HNO_3 were prepared at concentrations of 1, 10, 25, 50, 75, 100, and 150 ppb.

5.2.2 Batch Sorption Experiments

The effect of pH on Eu sorption to SRS soil in the presence and absence of natural organic matter was studied. For ease of comparison with previous actinide sorption on SRS soils work (Johnson (1995) and Clark et al. (1998)), experimental conditions of total Eu concentration of 10^{-6} M, a solids content of 20 g soil per liter (approximately 1 g clay per liter), and a pH range of 3 to 7 were chosen. A total organic carbon (TOC) concentration of 500 mg C/L of solution was used. It has been shown that TOC concentrations in natural forest litter leachate can be in the hundreds of mg C/L (Serkiz, 1991) and a value of 500 mg C/L was chosen as an upper limit for conditions expected in the burial trenches. Each set of experimental conditions (pH and carbon content) was prepared and analyzed in duplicate.

A 0.833-g sample of GC5 soil was added to each 42-ml polyallomer Oak Ridge centrifuge tube. To this, 20 ml of synthetic rainwater was added, and the tubes were placed on a linear shaker for one hour to create a soil suspension. The sorption experiments were initiated by adding 0.532 mL of the 10 ppm Eu stock, 0.0357 g of Suwannee OM, and synthetic rainwater to a final solution volume of 35 ml. The pH of each tube was then adjusted with standardized HNO_3 or NaOH. Clark et al. (1998) reported no loss of Eu to the tube walls, so a control group with no soil and OM was not prepared. Suspensions were then returned to the shaker for overnight equilibration. Previous work (Uhal, 1995) suggests that equilibrium will be reached under these timeframes. A kinetic study to confirm this equilibration time is currently in process. After equilibration, the supernatant was separated by centrifugation for 13 min at 16,000 g, followed by filtration through 0.45- μm membrane filters. The final equilibrium pH of the filtrate was measured. After pH measurement, each sample was preserved with ultrapure HNO_3 prior to Eu analysis.

5.2.3 Analytical Measurements

Eu Analysis

Europium concentrations in the solution phase were determined by graphite furnace AAS (Perkin Elmer 5100: HGA-600 furnace with Zeeman background correction). Furnace conditions were those recommended by the manufacturer. Measurements were made in duplicate or triplicate, and each analysis was performed twice.

pH

All pH measurements were made using a Fisher Accumet pH meter, model 50, equipped with a glass electrode, Ross model 8103. The pH meter was calibrated daily using standard buffer solutions (Fisher Scientific).

Total Organic Carbon

Total organic carbon was measured in those samples containing DOM using a Shimadzu TOC-5000 total organic carbon analyzer. The samples were diluted by a factor of 166.7.

6.0 Phase I - Results CDP Fate and Radionuclide Partitioning Studies

Section 6.1 of this report contains a review of previous work on the fate of CDP and partitioning of nuclides in the presence of these materials. This includes: (1) sorption of CDP on mineral surfaces, (2) actinide sorption to SRS soils, and (3) nuclide partitioning in the presence of CDP materials. The results of the most recent studies examining CDP organic surrogate sorption to the major clay mineral in near-surface soils in the GSA, kaolinite, and GSA soils are presented in Section 6.2. Finally, the results of U sorption to kaolinite and Eu sorption to GSA soils in the presence CDP organic surrogate material are in Section 6.3.

6.1 Literature Review

A significant volume of research exists on the sorption of naturally derived organic matter on a variety of mineral phases. Within this body of research, the following physicochemical factors are expected to influence DOM sorption to mineral surfaces:

- Fixed surface charge of solid.
- Compositional variations in solid phase (e.g., functional group density, bond strength, and configuration).
- Reactions at the solid surface that give rise to variations in surface charge (e.g., protonation and deprotonation reactions).

- Character and quantity of organic matter (e.g., polarity and molecular weight).
- Reactions of the organic matter with aqueous species (e.g., protonation/deprotonation and cation complexation reactions).

Several researchers (Sposito, 1984 and Murphy et al., 1990) have postulated a ligand-exchange mechanism for the sorption of naturally occurring DOM to mineral oxide surface. This postulated mechanism is described by the following three reactions:

Where SOH represents the surface hydroxyl group on the sorbent material.

Where $\text{O}=\text{C}(\text{O}^-)\text{DOM}$ represents a carboxyl group on the DOM molecule.

For this reaction pathway, the protonation step is thought to make the surface hydroxyl group more reactive (Equation 1), followed by outer-sphere carboxyl group complex formation (Equation 2), and, finally, ligand exchange of OH_2^+ for the carboxyl group resulting in an inner-sphere complex between the carboxyl group and the surface (Equation 3).

This reaction pathway is consistent with the general observations of DOM sorption to mineral surfaces. Where the fractional sorption of DOM to mineral surfaces and soils is generally; (1) pH-dependent, with a greater fraction of DOM sorbed at lower pH values; (2) dependent on total DOM concentration, with a greater fractional sorption at lower DOM concentrations; and (3) variable with respect to the character of both the sorbing surface and the organic matter. The pH-dependent sorption behavior is attributable, at least in part, to the protonation of the surface hydroxyl groups as the initial step in the ligand-exchange reaction pathway. At lower pH values, the concentration of protonated surface hydroxyl sites is greater, thereby allowing for a larger number ligand exchange reactions to occur. At a constant pH value the decreased in fractional DOM sorption with increasing DOM concentration can be attributed to the lower ratio of protonated hydroxyl surface binding sites to DOM molecules in solution.

Murphy et al., 1990 conducted studies to investigate the influence of organic matter character on DOM sorption to kaolinite and hematite. These mineral phases are also widespread in SRS soils (Johnson, 1995). The Murphy et al. study showed that for a particular organic matter source, fractional DOM sorption on hematite was substantially greater (e.g., approximately 20 percent at a pH of 5) than on kaolinite. This increased sorption on hematite was attributed to a greater surface hydroxyl density for hematite over kaolinite. Furthermore, this study also showed that the character of the organic matter, in particular molecular weight, influenced DOM sorption. Where increasing fractional sorption of DOM was correlated with increased molecular weight. Highest fractional sorption and, understandably, highest molecular weights were observed for organic material derived from terrestrial versus aquatic environments.

Previous work has also been conducted on the sorption of U (Johnson, 1995) and Eu (Clark et al., 1998) to GSA soils in the absence of organic matter. Both studies showed very similar sorption behavior. Typical of these systems, sorption behavior is nonlinear with respect to solution pH. At pH values below 4 the majority of the metal remains in solution phase. In the pH range between 4 and 6 the fractional sorption of the metal increases rapidly to near 100 percent where it remains to a pH of 7 (highest pH value investigated in these studies).

There has also been work specifically designed to study cellulose degradation products and their influence on radionuclide transport. Baston et al. (1992) investigated the effects of organic degradation products and gluconate on the sorption behavior of uranium (IV and VI), thorium (IV), and plutonium (IV) to certain geologic materials. They produced their own CDPs from a mixture of tissue, cement, and water, and rationalized the use of gluconate as a CDP surrogate to simplify the system. Gluconate is a readily available polyhydroxycarboxylic acid that has functional groups similar to those of CDP. The results of the Baston et al. (1992) study showed differing effects of actual CDP and gluconate on radionuclide sorption behavior. In all cases, gluconate had a greater effect on lowering the amount of radionuclide sorbed to the soil than actual cellulose degradation products. We, therefore, chose not to use gluconate as the organic matter surrogate in our studies.

A later study by Baston et al. (1994) extended the work described above to include the investigation of iso-saccharinate, in addition to gluconate, as a CDP surrogate. Analysis of degradation solution products formed by anaerobic processes using HPLC showed iso-saccharinate as an important constituent, as opposed to the aerobic solution that did not contain significant amounts of the compound. Their experiments examined the effects of the two surrogates and actual CDP concentrations at pH values of 8 and 12 on Pu and Th sorption to several geologic materials. In the case of Pu at pH 8, increasing gluconate concentration decreased sorption to a significant extent and increasing iso-

saccharinate concentration decreased sorption. Only the degradation products generated under aerobic conditions showed a significant decrease in sorption for Pu at pH 8. At pH 12, gluconate enhanced sorption to varying degrees, while iso-saccharinate decreased sorption for one soil type and enhanced sorption for the other. The anaerobic degradation products again decreased sorption, while the aerobic products did not. In the case of thorium, the trends were not as apparent. At a pH of 8, gluconate enhanced sorption up to the highest concentration, where the degree of sorption decreased. The aerobic degradation products only affected one soil type, increasing sorption when diluted, and decreasing sorption when used at full strength. At pH 12, increasing gluconate concentration only affected sorption in one soil type, decreasing sorption. A similar effect was seen with the actual degradation products.

The work of Serne et al. (1993) also investigated the sorption of certain radionuclide ions to Hanford sediments in the presence of their degradation products. Of all the ions studied, they found that only Co^{2+} , Sr^{2+} , and UO_2^{2+} sorption were affected by the presence of cellulose degradation products and TcO_4^- , I^- , CrO_4^{2-} , SeO_4^{2-} , Cs^+ , and NpO_2^+ .

6.2 Phase I - Results CDP Fate

Sorption experiments involving Suwannee River organic isolate (CDP surrogate) and two solid phases, kaolinite and SRS soil, were conducted as part of this study. The results of these experiments are described in Sections 6.2.1 and 6.2.2 for kaolinite and SRS soil respectively.

6.2.1 Phase I – Sorption of DOM to Kaolinite

The sorption of Suwannee River DOM to kaolinite was examined at initial DOM concentrations of 10 and 30 mg C/L over a pH range from approximately 3 to 7. The results of these experiments are summarized in Figure 4. Where the fractional sorption is the mass of carbon sorbed divided by the total mass of carbon added to the system.

Over the range of experimental conditions the fractional sorption of DOM to kaolinite varied from 3 to 60 percent. Consistent with previous research (e.g., Murphy, *et al.* 1990), natural DOM sorption exhibits decreased sorption with increasing pH and relatively greater fractional sorption in systems with lower DOM concentration.

6.2.2 Phase I – SRS Soil/DOM System

The sorption of Suwannee River DOM to GSA soil was examined at an initial DOM concentration of 500 mg C/L over a pH range from approximately 3 to 6.

The intent of this experiment was to evaluate europium binding to an actual SRS soil under an expected upper limit of DOM concentration. Unlike the results for kaolinite-DOM experiments described above, carbon sorption measurements were made in the presence of added Eu. The results of these experiments are summarized in Figure 5. Where the fractional sorption is the mass of carbon sorbed divided by the total mass of carbon added to the system.

Over the range of experimental conditions the fractional sorption of DOM to kaolinite varied from 2 to 20 percent. Consistent with the kaolinite-DOM results, natural DOM sorption exhibits decreased sorption with increasing pH and relatively greater fractional sorption in systems with lower DOM concentration.

6.3 Phase I - Results Radionuclide Partitioning Studies

Sorption experiments involving U to kaolinite and Eu to SRS soil in the presence and absence of Suwannee River organic isolate (CDP surrogate), were conducted as part of this study. The results of these experiments are described in Sections 6.3.1 and 6.3.2 for U sorption to kaolinite in the presence and absence of CDP surrogate respectively and Sections 6.3.3 and 6.3.4 for Eu sorption to SRS soil in the presence and absence of CDP surrogate respectively.

6.3.1 Phase I – Sorption of U to Kaolinite

As a basis to evaluate the influence of the presence of CDP surrogate on uranium sorption, uranium sorption experiments were conducted in the absence of Suwannee River organic matter. The sorption of uranyl ion (UO_2^{2+}) to kaolinite was examined at an initial uranyl concentration of 10^{-6} M and over a pH range from approximately 2 to 7. The results of these experiments are summarized in Figure 6.

The general shape of this sorption isotherm, where low fractional sorption occurs at low-pH values with a rapid sorption increase as pH increases, is typical of cation sorption to metal oxy-hydroxides. Mechanistically, the solid surface is more positively charged at low-pH values due to protonation of the surface hydroxyl binding sites and thus acts to more effectively repulse the binding of positively charged aqueous cations. The concentration based K_d of 50 L/Kg used in the previous PA modeling (where K_d is defined as concentration solid/concentration aqueous) is also plotted on this graph at a fractional sorption of 99.7 percent and exhibits no pH dependence. For SRS soils where a typical unperturbed pH range is on the order of 4 to 6 (Findley, 1998), the fractional sorption from the 0.45- μ filtered laboratory data ranges from 30 to 99 percent over this pH range.

For samples filtered through a standard 0.45- μ filter, the pH value at 50% uranyl sorption (pH_{50}) for this experiment was about 4.5 and is consistent with similar uranyl sorption to kaolinite data reported by Payne et al. (1992). Interestingly, the pore size of the filter used to separate solids from liquids in the experiment appears to have a significant impact on the calculated fraction sorbed. The decrease in uranium from the solution phase of samples filtered using a 0.2- μ filter suggests significant colloid loading and contaminant association with colloidal material in these experiments. Further experiments are planned to further examine these results.

6.3.2 Phase I – Sorption of U to Kaolinite/DOM

To evaluate the influence of CDP surrogate on uranium sorption to kaolinite, uranium sorption experiments were conducted at: initial DOM concentrations of 10 and 30 mg C/L; an initial uranyl concentration of 10^{-6} M; and over a pH range from approximately 2.5 to 7.0. The results of these experiments are summarized in Figure 7 and the uranyl-kaolinite isotherm in the absence of OM is plotted for reference.

The effect of the added organic matter for both added OM concentrations at pH values below 4.5 was to increase the fractional sorption (reduce mobility) of uranyl when compared to experiments without the OM. This is thought to be the result of forming partially charged neutralized kaolinite surface by sorbed organic matter. The resulting OM sorbed surface having a higher affinity for aqueous cations than the positively charged kaolinite surface.

At pH values above 4.5, the effects of OM on the fractional sorption of uranyl were dependent on the concentration of added OM. At the low OM concentration (10 mg C/L), fractional sorption of uranyl was enhanced over the entire pH range. At the higher OM concentration (30 mgC/L) and pH values above 4.5, uranyl sorption was suppressed between 40 and 50 percent. As the fractional sorption of DOM decreases with increasing DOM concentration (see Section 6.2.1), the reduced uranyl sorption in this system could be explained by increased aqueous complexation of uranyl ions by DOM.

6.3.3 Phase I – Sorption of Eu to SRS Soil

Our research examined the sorption of Eu^{3+} to SRS soil from the GSA. These data form a basis to evaluate the influence of the presence of CDP surrogate on europium sorption on SRS soil and are summarized in Figure 8.

The sorption edge reported by Clark et al (1998) approximately covered the same fraction of Eu sorption, but was less steep. Their sorption edge occurred between pH 3 and 5. It has been shown, however, that the actual shape of the sorption edge can be sensitive to experimental conditions (Schunthless and

Huang 1990, and Spark et al. 1995). Decreasing the metal to sorbent ratio was shown to increase the slope of the sorption edge. In the Clark et al., (1998) experiments, the metal to sorbent ratio was lower than in the current experiments. The reason for this behavior is currently not known. Further experiments are being planned to examine this behavior.

The general shape of the sorption isotherm for this system is similar to the kaolinite uranyl system (see Figure 6). For similar experimental conditions, 10^{-6} M Eu and lowest backing electrolyte concentration, the Eu isotherm exhibits enhanced sorption at low pH values with a pH_{50} of less than 3.3 as compared 4.5 for kaolinite. This enhanced binding is at least in part due to the higher charge density of Eu^{3+} over UO_2^{2+} . Additionally, as is typical of sorption isotherms of whole soils, the sorption edge is less steep than those typical of cation sorption to simple metal oxy-hydroxides.

Above pH 7, the sorption behavior of Eu is less smooth. This may be caused by the formation of a soluble Eu-hydroxyl (OH) complex that forces some of the sorbed Eu back into solution. The formation of an Eu-OH complex is thermodynamically favored at pH values above 7. Baes and Mesmer (1986) reported that $\text{Eu}(\text{OH})_3$ has a $\log K_{\text{sp}}$ of 16.5 and the $\log K_{\text{Eu}(\text{OH})_2^+}$ is 7.8 and Lee et al. (1995) have shown evidence for the formation of an Eu(III)-OH complex above pH 6 in aqueous solution.

6.3.4 Phase I – Sorption of Eu to SRS Soil/DOM

The results of the Eu adsorption experiments in the presence of 500 mgC/L of Suwannee River OM are presented in Figure 9. Unlike other sorption experiments presented in this study, sorption of Eu in this ternary system is much less sensitive to solution pH.

In the uranyl sorption at 30 mg C/L there was an initial increase in sorption up to a pH of 4, where the curve leveled out and the fraction of uranium adsorbed varied between 0.45 and 0.55. A similar effect was shown in the data of Fairhurst et al (1995) for the adsorption of Eu to kaolinite in the presence of Aldrich humic acid. This study used a lower Eu concentration (10^{-9} M) and higher sorbent concentration (2g clay/L). The difference between the current experiment and the two others probably stems from the high concentration of organic matter used in the current experiment.

There is some evidence supporting these results. The study of Allard et al (1989) investigated the sorption of Americium on alumina in the presence of humic acid isolated from a surface water. At an Am concentration of 9.97×10^{-9} M, ionic strength of 0.1 and 0.01, and a humic concentration of 10 mg/L, the system showed a gradually decreasing degree of sorption of Am to the alumina as a function of decreasing pH.

Further experiments are planned to examine the influence of lower DOM concentrations on the sorption of Eu to SRS soil.

7.0 Phase I - Summary and Conclusions

The previous cellulose degradation modeling effort (Serkiz and Myers, 1996) recognized the complexities of the physicochemical processes of subsurface nuclide transport in the presence of natural organic matter. As a result of these complexities, a number of assumptions were made. These included:

- The concentration based K_d approach used in current PA modeling can adequately describe nuclide sorption to SRS soils;
- Sorption of organic matter to SRS soils was constant and equal to 20 percent of the total organic carbon (after Murphy et al., 1990);
- Low molecular weight organic acids like citric acid can be used to approximate the behavior of cellulose degradation products; and
- The metal binding behavior of the sorbed organic matter could be approximated from the stability constant of the metal and organic matter in solution (i.e., no synergistic effects between the solid phase (kaolinite or whole soil) and the sorbed organic matter.

Figures 6 and 8 show the nonlinear sorption behavior of uranyl and Eu (III) as a function of pH in the absence of organic matter. At higher pH values, where the fractional sorption of the metal approaches 100 percent and exhibit only small changes sorption behavior in response to pH, a concentration based K_d approach appears to provide a good fit to the experimental data. For uranyl sorption, where the pH_{50} is about 4.5, large changes in sorption behavior are expected to occur with small changes in the natural pH. Cellulose will degrade to form natural organic acids and these materials are capable of reducing the pH of the system. The pH reduction caused by the generation of these organic acids could, therefore, significantly alter the fractional sorption of the nuclide of interest as well as the major ion chemistry of the system. The influence of CDP on the alteration of pH and major ion chemistry will, therefore, be examined in subsequent phases of this work.

These experiments and much previous research show that sorption of natural OM varies as a function of pH and total carbon content (see Figures 4 and 5). Sorption increasing with decreasing organic carbon content and decreasing pH. Over the range of experimental conditions examined in this study (pH 3 to 8 and DOM concentration from 10 to 500 mg C/L) fractional sorption of organic matter varied from several percent to about 60 percent. These effects were systematic and should be accounted for in future modeling phases of this work.

Previous research by Baston et al. (1992) used gluconate as a CDP surrogate and compared its influence on actinide sorption to actual CDP generated in laboratory experiments. In all cases, gluconate had a greater effect on lowering the amount of radionuclide sorbed to the soil than actual cellulose degradation products. We, therefore, chose to use naturally occurring DOM isolated from the Suwannee River as the organic matter surrogate in our studies. Its similarities and differences to actual CDP will be evaluated in Phase II of this work.

In the presence of naturally occurring organic matter (see Figures 7 and 9) a significant effect of pH and organic matter concentration was observed for U and Eu sorption. Over the range of experimental conditions examined in this study the following summarizes the influence of CDM surrogate on U and Eu sorption (i.e, decreased mobility):

	<u>Low Organic</u>	<u>High Organic</u>
<u>Low pH</u>	↑ sorption	↑ sorption
<u>High pH</u>	no effect	↓ sorption

Specifically, for uranyl at pH values below 4.5 the effect was to increase the fractional sorption (reduce mobility) of uranyl when compared to experiments without the OM and at pH values above 4.5, the effects of OM on the fractional sorption of uranyl were dependent on the concentration of added OM. At the low OM concentration (10 mg C/L), fractional sorption of uranyl was enhanced over the entire pH range relative to the high OM experiments. At the higher OM concentration (30 mgC/L) and pH values above 4.5, uranyl sorption was suppressed between 40 and 50 percent. As the fractional sorption of DOM decreases with increasing DOM concentration (see Section 6.2.1), the reduced uranyl sorption in this system could be explained by increased aqueous complexation of uranyl ions by DOM. For Eu sorption in the presence naturally occurring OM, as was the case for uranyl at the high DOM concentration, enhanced sorption at the very lowest pH values (c. pH of 3) and was suppressed by about 50 percent at higher pH values. While it is clear that the sorbed organic surface does not exhibit the same metal binding behavior as the aqueous specie, additional data interpretation and model development will be necessary to explain these effects.

8.0 References

- Allard B., Moulin V., Ballo L., Tran M.T. Stammose D., (1989). Americium Adsorption on Alumina in the Presence of Humic Materials. *Geoderma*, Vol.44, 181-187.
- Baes C.F., Jr. and Mesmer R.E., (1986). The Hydrolysis of Cations. 2nd ed. Robert E Krieger Publishing, Malabar, Fl.
- Baston, G.M.N., Berry, J.A., Bond, K.A., Brownsword, M., and Linklater, C.M. (1992). Effects of Organic Degradation Products on the Sorption of Actnides. *Radiochimica Acta*, Vol. 58-59, 349-356.
- Baston G.M.N., Berry J.A., Bond K.A., Boulton K.A., Linklater C.M. (1994) Effects of Cellulosic Degradation Product Concentration on Actinide Sorption on Tuffs From the Borrowdale Volcanic Group, Sellafield, Cumbria. *Radiochim. Acta*. Vol 66/67, 521-526.
- Choppin G.R. (1989). Soluble Rare Earth and Actinide Species in Seawater. *Mar. Chem.* Vol. 28, 19-26.
- Clark S. B., Bryce A. L., Lueking, A., Gariboldi J., Serkiz S. M., (1998) *Factors Affecting Trivalent f-element Adsorption to an Acidic Sandy Soil* in Adsorption of Metals by Geomedia, Variables, Mechanisms, and Model Applications (E. A. Jenne, editor), Academic Press.
- Cozzarelli, I.M., Baedecker, M.J., Eganhouse, R.P., Goerlitz, D.F. (1994). The Geochemical Evolution of Low-Molecular-Weight Organic Acids Derived From the Degradation of Petroleum Contaminants in Groundwater. *Geochimica et Cosmochimica Acta*, Vol. 58, 863-877.
- Fairhurst A.J., Warwick P., Richardson S. (1995). The Effect of pH on Europium-Mineral Interaction in the Presence of Humic Acid. *Radiochim. Acta*. Vol. 69, 103-111.
- Findley, M. (1998) Characterizing the Environmental Availability of Trace Metals in Soils at the Savannah River Site. Master's Thesis. Clemson University, Clemson, SC.
- Johnson, N.A. (1994). Clay Mineralogy of the Surficial Aquifer and Confining System, F- and H-Area Seepage Basins, Savannah River Site. Phase 1 - Final Report. University of Florida, Dept. of Geology.
- Johnson, W. H. (1995) Sorption Models for U, Cs, and Cd on Upper Atlantic Coastal Plain Soils. Ph.D. Thesis. Georgia Institute of Technology, Atlanta, GA.

Krauskopf, K. B. (1986). Thorium and Rare Earth Metals as Analogues for Actinide Elements. *Chem. Geol.* 55:323-335.

Ledin A., Karisson S., Düker A., Allard B. (1994). The Adsorption of Europium to Colloidal Iron Oxy-hydroxides and Quartz – The Impact of pH and an Aquatic Fulvic Acid. *Radiochim. Acta*, vol.66/67, 213-220.

Lee J.J. and Weber D.E., (1979). Effects Of Sulfuric Acid Irrigation on Major Cation and Sulfate Concentration on Water Percolating through Two Model Hardwood Forests. *J. Environ. Qual.*, Vol. 11, 57-64.

Lee H.B., Yeong J.P., Moon H., (1995). Identification Of Europium(III) Hydroxide Formation By Eu (III) Luminescence Spectroscopy. *Bull. Korean Chem. Soc.*, Vol. 16, 654-657.

Mattigod, S.V., J.A. Frampton, and C.H. Lim, (1985) Effect of Ion-Pair Formation on Boron Adsorption by Kaolinite, *Clays and Clay Minerals*, Vol. 33, 433-437.

MMES (Martin Marietta Energy Systems), EG&G Idaho, Inc., and Westinghouse Savannah River Company, (1994). Radiological Assessment for the E-area Vaults Disposal Facility (U). Report No. WSRD-RP-94-218, Rev. 0. WSRC, Aiken, SC.

Murphy, E.M., Zachara, J.M. and Smith, S.C. (1990). Influence of Mineral-Bound Humic Substances on the Sorption of Hydrophobic Organic Compounds. *Environ. Sci. Technol.*, Vol.24, 1507-1516.

Perdue, E.M. and Gjessing, E.T. (1990). *Dahlem Workshop Reports: Organic Acids in Aquatic Ecosystems*. Wiley & Sons, New York.

Schunthless C.P., Huang C.P., (1990). Adsorption of Heavy Metals by Silicon and Aluminum Oxide Surfaces on Clay Minerals. *Soil Sci. Soc. Am. J.* Vol. 54, 679-668.

Serkiz S.M., (1991). Factors Affecting the Binding of Protons and Metal Ions to Naturally Occurring Dissolved Organic Matter. Doctoral Thesis, Georgia Institute of Technology.

Serkiz S. M. and Perdue E. M., (1990) Isolation of Dissolved Organic Matter From the Suwannee River Using Reverse Osmosis. *Wat. Res.*, 24, 911-916.

Serkiz S. M. and Myers J.L., (1996). Additional Information for E-area Vault Performance Assessment, Appendix I "Suspect Soil Performance Analysis" – Results of Modeling the Effects of Organic Matter on the Mobility of Radionuclides as it Relates to the Disposal of Wood Products in E-Area Slit Trenches. Westinghouse Savannah River Company. WSRC-TC-98-00049. Aiken, SC.

Serne, R.J., Conca, J.L., LeGora, V.L., Cantrell, K.J., Lindenmeier, C.W., Campbell, J.A., Amonette, J.E. and Wood, M.I. (1993). Solid-Waste Leach Characteristics and Contaminant-Sediment Interactions, Volume 1: Batch Leach and Adsorption Tests and Sediment Characterization. Report No. PNL-8889 Vol. 1. PNL, Richland, WA.

Spark K. M., Johnson B. B., Wells J. D., (1995). Characterizing Heavy-Metal Adsorption on Oxides and Oxy-hydroxides. *Europe. J. of Soil Sci.* Vol. 46, 621-631.

Sposito, G. (1984) The Surface Chemistry of Soils. Oxford University Press: New York.

Strom, R. N. and Kaback, D. S. (1992). SRP Baseline Hydrogeologic Investigation: Aquifer Characterization. Groundwater Geochemistry of the Savannah River Site and Vicinity. Report No. WSRC-RP-92-450. WSRC, Aiken, SC.

Stumm W. and Morgan, J.J. (1981). *Aquatic Chemistry*. Wiley & Sons, New York.

Thurman, E.M. (1985). *Organic Geochemistry of Natural Waters*. Kluwer Academic, Hingham, MA.

Uhal H. T., (1996). Uranyl Sorption by a Mixed Kaolinite and Naturally Occurring Organic Matter System. Special project presented to the faculty at Clemson University, Clemson, SC.

9.0 Tables

TABLE 1
SAMPLE MATRIX FOR DOM ON KAOLINITE

Sample ID	Target pH	Tube Contents
81-1	8.0	42 ml kaolinite suspension
81-2	4.0	1 ml DOM solution 41 ml DI water
81-3	8.0	1 ml DOM solution 41 ml kaolinite suspension
81-4	7.5	1 ml DOM solution 41 ml kaolinite suspension
81-5	7.0	1 ml DOM solution 41 ml kaolinite suspension
81-6	6.5	1 ml DOM solution 41 ml kaolinite suspension
81-7	6.0	1 ml DOM solution 41 ml kaolinite suspension
81-8	5.5	1 ml DOM solution 41 ml kaolinite suspension
81-9	5.0	1 ml DOM solution 41 ml kaolinite suspension
81-10	4.5	1 ml DOM solution 41 ml kaolinite suspension
81-11	4.0	1 ml DOM solution 41 ml kaolinite suspension
81-12	7.0	42 ml DI water

TABLE 2

SAMPLE MATRIX FOR URANYL KINETICS

Sample ID	Target Time	Target pH	Tube Contents
99-A1	5 minutes	3.05	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-A2	30 minutes	3.05	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-A3	1 hour	3.05	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-A4	2 hours	3.05	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-A5	4 hours	3.05	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-A6	16.7 hours	3.05	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-A7	16.7 hours	3.05	1 ml uranyl nitrate solution 41 ml DI water
99-A8	16.7 hours	3.05	1 ml DI water 41 ml DOM-kaolinite mixture
99-B1	5 minutes	7.25	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-B2	30 minutes	7.25	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-B3	1 hour	7.25	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-B4	2 hours	7.25	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-B5	4 hours	7.25	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-B6	16.7 hours	7.25	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
99-B7	16.7 hours	7.25	1 ml uranyl nitrate solution 41 ml DI water
99-B8	16.7 hours	7.25	1 ml DI water 41 ml DOM-kaolinite mixture

TABLE 3

SAMPLE MATRIX FOR URANYL WITH DOM ON KAOLINITE

Sample ID	Target pH	Tube Contents
12-A1 and 12-B1	3.0	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A2 and 12-B2	3.5	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A3 and 12-B3	4.0	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A4 and 12-B4	4.5	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A5 and 12-B5	5.0	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A6 and 12-B6	5.5	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A7 and 12-B7	6.0	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A8 and 12-B8	6.5	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A9 and 12-B9	7.0	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A10 and 12-B10	7.5	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A11 and 12-B11	8.0	1 ml uranyl nitrate solution 41 ml DOM-kaolinite mixture
12-A12 and 12-B12	n/a	1 ml DI water 41 ml DOM-kaolinite mixture
12-A13 and 12-B13	n/a	1 ml uranyl nitrate solution 41 ml DI water

TABLE 4
SOLUTION OXIDATION-REDUCTION POTENTIALS

Sample ID	Potential Before	Potential After
99-A1	478.5 mV	490.1 mV
99-B1	339.3 mV	359.3 mV
99-A8 (blank)	478.5 mV	482.3 mV
99-B8 (blank)	339.3 mV	362.5 mV
112-A2	468.6 mV	459.0 mV
112-B3	468.6 mV	439.3 mV
131-20	370.1 mV	350.4 mV
131-21	370.1 mV	351.6 mV

Figure 1. Typical Porewater DOM Concentration Profile From Thurman, 1985

Figure 2. Functional groups present on a complex DOM molecule (from Thurman, 1985)

Figure 3. Conceptual SRS Soil Grain

Figure 4 - Fractional Sorption of Suwannee River DOM to Kaolinite

Figure 5 - Fractional Sorption of Suwannee River DOM to GSA Soil

Figure 6 - Fractional Sorption of Uranium to Kaolinite

Figure 7 - Fractional Sorption of Uranyl to Kaolinite in the Presence of Organic Matter

Figure 8 - Fractional Sorption of Europium In the Absence of OM

Figure 9- Fractional Sorption of Europium with 500mgC/L Suwannee River OM

**WESTINGHOUSE SAVANNAH RIVER COMPANY
SAANNAH RIVER TECHNOLOGY CENTER**

December 20, 1998

Distribution:

**B. T. Butcher, 773-43A
W. E. Stevens, 773-A
W. L. Tamosaitis, 773-A
W. T. Goldston, 705-3C
Heather Holmes-Burns, 724-9E
D. F. Sink, 724-15E
M. W. Lewis, 724-7E
P. I. Hudson, 705-3C
Cindy Lee, Clemson
Dave Knaub, Clemson
D. I. Kaplan, 773-A
S. M. Serkiz, 773-A
E. L. Wilhite, 773-43A
J. R. Cook, 773-43A**