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Impact of Alteration Phase Formation and Microbial Activity on the Fate and Transport of the Actinides and Fission Products: Alteration Phase Analysis

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DOCUMENT CHANGE NOTICE
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DOCUMENT TITLE: **Impact of Alteration Phase Formation and Microbial Activity on the Fate and Transport of the Actinides and Fission Products: Alteration Phase Analysis**

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Identify applicable affected page, section, paragraph, attachment, exhibit, table, figure, or other:

In 2.0, Subtask 3, delete the 2nd paragraph. Page 4
In 2.0, Phase 2, 1st paragraph, 1st sentence delete: "manganese oxyhydroxides", "manganite".
In 2.0, Phase 2, 1st paragraph, 2nd sentence delete: ", such as clay like phases observed during the dissolution of borosilicate glass and the mineral alteration phases formed during the dissolution of uranium oxide (schoepite, etc.)."
In 2.0, Phase 2, 1st paragraph, 6th sentence delete: "Pu, Np" Page 5
In 2.0, Phase 2, 1st paragraph, delete the last two sentences.

In 6.0, 2nd paragraph delete sentences 2-4. Page 7

In 9.0, delete "5. IPLV-011, "Measurements of Major Cations in Water Samples by the Flame Atomic Absorption Spectroscopy System."" and "7. IPLV-030, "Preconcentration of Rare Earth Elements.""
Page 7

Approved by:

PI: [redacted] Date: 11/6/06
(Signature)
Print name:

QA Manager: [redacted] Date: 11-6-06
(Signature)
Print name: [redacted]

QA Manager evaluated acceptability that it does not violate quality requirements, and for impacts to other procedures; signature above documents this evaluation as successfully completed.

Attach this DCN as first page of hard copies of document, if any.

University and Community College System of Nevada (UCCSN)
Scientific Investigation Plan (SIP)

Task Title:	**Impact of Alteration Phase Formation and Microbial Activity on the Fate and Transport of the Actinides and Fission Products: Alteration Phase Analysis**
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REVISION HISTORY

Revision Number	Effective Date	Description and Reason for Change
0	01/06/05	Initial issue.

1.0 Scope and Objectives

The study of the behavior and movement of radionuclides in the environment is significant to many projects of interest to Southern Nevada, especially for the proposed Yucca Mountain Repository, as well as to the nation-wide issues of radiological releases from a variety of scenarios. Understanding and predicting the release, transport, and fate of radionuclides, particularly the actinide elements, in the Mojave/Great Basin geology is an extremely challenging, multi-faceted problem. In support of the national program to deepen our understanding of the behavior of radionuclides in the environment and to better predict the performance of a geological repository at Yucca Mountain, researchers at UNLV, under a cooperative agreement between and UNLV Research Foundation and the U.S. Department of Energy (#DE-FC28-04RW12237), will examine two key fate and transport issues: the potential impact of microorganisms and the impact of the formation of alteration phases due to the corrosion of the waste package and waste forms on the chemistry, fate, and transport of radionuclides released from the site. Task ORD-RF-01 (SIP-UNLV-046) is focused on the influence of microorganisms. Task ORD-RF-02 (SIP-UNLV-045) involves surface complexation and solid dissolution studies. This task, titled Impact of Alteration Phase Formation and Microbial Activity on the Fate and Transport of the Actinides and Fission Products: Alteration Phase Analysis, entails method development and elemental characterization of select alteration phases generated in Task ORD-RF-02. All of this work is subject to QARD and University and Community College System of Nevada (UCCSN) Quality Assurance (QA) Program requirements.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a powerful analytical technique that focuses a laser beam on a target and sweeps ablated material into an ICP-MS where elemental and isotopic information can be obtained. LA-ICP-MS has become the method of choice for the determination of long-lived radionuclides in solid nuclear waste or contaminated environmental samples. The spot size of the laser (and resultant ablation craters) can be adjusted down to a few micrometers in diameter making the method particularly effective in microanalysis applications. The laser can target minute features of subsurface rock, such as secondary minerals, and repetitive sampling (firing) can provide depth profiles of the elemental and isotopic composition of samples.

The work covered in this SIP will focus on the development and application of LA-ICP-MS for the direct analysis of the alteration phases. The objective is to examine the localized chemistry of the alteration phase itself as well as the sorption or inclusion of the actinides into the alteration phases. Other corroborative techniques, such as the electron microprobe and the transmission electron microscope (TEM) may also be employed. Radionuclides can sorb or enter the alteration phase either through inclusion during the dissolution of the waste form (fuel pellet, borosilicate glass, etc.) or via sorption to the alteration phase from groundwater. We will work closely with Task ORD-RF-02 investigators in selection of samples and experimental parameters. The goal is to provide data and insight to Task ORD-RF-02 investigators, who will use the information to examine sorption and desorption behavior of key radionuclides onto the alteration phases formed during the corrosion of the waste forms, waste package, and structural

materials. This is information will shed light on the potential speciation, transport and fate of actinides in the repository environment.

2.0 APPROACH

Phase 1: Preparation, Training and Method Development

Subtask 1: Complete SIP, personnel QA training, and selection and purchase of instrumentation. A Time-Of-Flight (TOF) mass analyzer was chosen because it is well-suited for multi-element analysis of fast transient signals.

Subtask 2: The laboratory will be prepared and new instrumentation installed. The LA system will be coupled to the new ICP-TOFMS and the analysts will be trained on the operation and software of the new system.

Subtask 3: This subtask involves method development and scoping work. Unlike solution analyses where generally there is ample sample volume to work with, the analytes of interest in this study may only exist in a thin film on the surface of the sample. To address this issue, we will conduct scoping experiments to maximize sensitivity. This may include changing instrumental parameters and using a large and/or moving spot size. A QA-approved standard (if available), in-house sample or synthetically prepared matrix containing a thin film of radionuclides will be used to conduct optimization experiments (systematically varying relevant parameters such as sweep gas rate, torch position, RF power, etc.). We will also explore adding small quantities of He and possibly other gases to the sweep gas to enhance transport properties. Molecular ions can also limit the performance of LA-ICP-MS due to isobaric interferences with analytes. It has been shown that oxide formation increases with increasing carrier gas flow rate possibly because ablated oxides are not completely dissociated in the plasma (Becker 2000). We will also vary gas flow rates, along with RF power, sampling depth and other parameters to minimize molecular ion formation that interfere with the analysis of actinides such as ^{239}Pu.

~~One critical factor in this analysis is the particle size distribution (psd) of the ablated material. Particles greater than ~1.0 µm in diameter do not fully dissociate and ionize in the typical plasma of an ICP. Larger particles can lead to severe matrix effects and instrumental drift due to clogging of interface cones. Therefore, LA should ideally yield a relatively uniform psd with sizes below this cutoff. We propose to study the psd stemming from the ablation of samples under varying laser conditions (e.g., wavelength, pulse rate, spot size). Samples of ablated material will be collected on a filter downstream of the ablation cell and analyzed by TEM. The goal of this scoping work is to determine optimal settings for producing the most stable signal and the greatest sensitivity. If large particles remain an issue, it may be necessary to employ some kind of chamber or filter, such as centrifugal device, to remove large particles from the gas stream. However, removing only the large particles may cause a bias in the results, particularly if the sample is not homogenous. A robust plasma is also necessary to disintegrate particles so settings such as RF power will also be evaluated.~~

See DCN #1

Whereas the scoping studies highlighted above are expected to yield important information, which will be included in the final report for information purposes, they will also be used to develop a new IPLV to obtain qualified data. The IPLV will be used to obtain quantitative elemental concentration data from unaltered mineral and alteration phase samples using LA-ICP-TOFMS, the focus of Phase 2.

Phase 2: Alteration Phase Analysis

Study of the sorption of the actinides and fission products to alteration phases will start with the same well-defined mono-mineralic phases (e.g., ~~manganese oxyhydroxides,~~ goethite, ~~manganite~~) investigated in the surface complexation task (ORD-RF-02). As the project continues, the technique will be applied in the investigation of more complex alteration phases, ~~such as clay-like phases observed during the dissolution of borosilicate glass and the mineral alteration phases formed during the dissolution of uranium oxide (schoepite, etc.).~~ Specific samples to be analyzed cannot be determined at this time because they will depend on the results of both the scoping studies and Task ORD-RF-02. Samples from Task ORD-RF-02 will be transferred via chain-of-custody procedures. Identification and control of samples will follow QAP-8.0. LA-ICP-MS and possibly the electron microprobe and TEM will be used to examine the potential inclusion of the actinides (e.g., U, ~~Pu, Np)~~ in the alteration phase samples during the dissolution of actinide-bearing waste forms. ~~Profiles of elemental composition with depth from sample surface will be established. The goal is to characterize the test samples by quantifying select elements (e.g., Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) and radionuclides in the alteration phases.~~

See DCN #1

Both the scoping studies and subsequent work using an approved IPLV will be documented in the scientific notebook. Any special environmental conditions or controls will be described in the corresponding IPLV or scientific notebook. Any processes not addressed in the IPLV will be documented in the scientific notebook. The skills of the personnel contributing to the project are outlined in their position descriptions. There are no special training requirements for this work beyond the education and experience requirements of each employee's position description. There is no plan to conduct field surveys as part of this work.

Phase 3: Task Close-Out

The final phase of the project involves closing out the task and includes report writing and technical and QA reviews.

3.0 SCHEDULE OF WORK

The research will be conducted in 3 phases. Phase 1 involves preliminary scoping work (~6-8 months) to develop and optimize the LA technique for the various sample matrices. There will be no qualified data associated with this scoping work; it is for informative purposes only and may be used to establish a new IPLV for LA-ICP-MS. In phase 2, we will use the methods developed in phase 1 to characterize a number of samples generated from the surface complexation task. Phase 3 will focus on those items necessary for closing out the task, including all the QA reviews and preparation of the final report.

Since the majority of the work being conducted involves method development, there is no set schedule. Reports summarizing the progress of this study will be submitted quarterly. In accordance with QAP-3.6, Q data will be submitted to the UCCSN Technical and Electronic Data specialist for entry into the UCCSN Technical Data Archive (TDA). Q submissions will consist of data that have been verified using the check lists included in the appropriate instrument IPLV and for which the associated scientific notebook has been reviewed both for QA and technical content. QA records will be submitted to the UCCSN Records Office within 60 days following the completion of the project.

4.0 INTERFACE CONTROLS

External Interfaces
DOE Technical Representative: Abe Van Luik
Internal Interfaces

Principal Investigator:	Klaus Stetzenbach
Co-PI:	James Cizdziel
Investigators:	Vernon Hodge
Analysts:	Caixia Guo, Kaz Lindley, Tatjana Jankovic, Julie Bertoia, Jeanette Daniels
Students:	Joseph Lloren, David Edwards

5.0 EQUIPMENT AND INSTRUMENTATION

The specific equipment used for each measurement will be documented in the scientific notebook or other QA record. Documentation will include the instrument manufacturer, model, and serial number. The calibration, accuracy, and precision requirements for all equipment are to be described in the corresponding IP. Analytical instruments will be calibrated before each use (where applicable). All Measurement and Test Equipment (MT&E) will be protected by storage in a locked laboratory or cabinet to prevent loss and tampering.

The ICP-TOFMS will be calibrated in-house. Other equipment that may be used includes analytical balances and pipettors. Balances will be calibrated annually by Bechtel .The reference mass set used to check working mass sets is calibrated every two years by an organization on the Qualified Supplier List (QSL). Calibrations of Pipettors are checked annually. Calibrations and calibration checks will be performed by HRC staff or by an organization on the QSL. A JEOL-8900 Electron Probe Microanalyzer, JEOL JSM-5600 Scanning Electron Microscope (SEM), and a Transmission Electron Microscope (TEM), all housed at the UNLV campus, may also be used to provide images and qualitative information on the distribution of elements on sample surfaces.

6.0 STANDARDS/PROCUREMENTS/SUBCONTRACTS

All standards used must come from NIST, a qualified supplier, or the basis of acceptance reviewed and approved by the QA Manager in accordance with QAP-12.0 “Control of Measuring and Test Equipment,” before standards are used for quality affecting work.

~~To the extent possible, we will use solid reference materials from the USGS, NIST, NBL or other sources to calibrate and monitor accuracy during analyses. If a suitable standard is not available (i.e., similar matrix), we will attempt calibration by introducing liquid standards into a desolvating nebulizer and using the dry aerosol to flush the ablation cell. In short, the idealized mixing of the nebulized calibration solutions with laser ablated material will be used in a matrix matched standard addition calibration procedure.~~ Note: For samples that readily ablate (e.g., silicates) as apposed to melt and evaporate (pure metals) there is evidence that little isotopic fractionation occurs in the ablation process but rather stems form the ICP process and the changing psd of ablated material.

See DCN #1

Calibration items and services are procured in accordance with QAP-7.0. No subcontractors are expected to be used in this work.

7.0 SOFTWARE and MODELS

No software will be developed in this study. The software packages used in this study include 1) The analytical instrumentation software used for data acquisition, and 2) Spreadsheet software such as Quattro Pro or Excel for data reduction. Any macros used in Excel, etc. will be qualified and documented. Use of the analytical instrumentation data acquisition and spreadsheet software will be documented or referenced, along with the specific version used, in the instrument scientific notebook or other QA record. Control of electronic data is addressed in each IPLV that involves electronic data management, primarily instrument system IPLVs. No models will be developed for or used during this study.

8.0 PROCUREMENTS and SUBCONTRACTS

Calibration standards will be purchased directly from NIST or qualified vendors. The basis for acceptance of any standards that are not available from a qualified supplier will be documented in the scientific notebook. Balances and pipettors will be calibrated annually by a qualified supplier.

9.0 IMPLEMENTING PROCEDURES

1. IPLV-003, “Analytical and Top Loading Balance Use”.
2. IPLV-008, “Measurements of Anions in Water Samples by the Ion Chromatography System.”
3. IPLV-8.3, “Groundwater sample collection and control”
4. IPLV-009, “Measurement of Trace Elements in Water Samples by the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).”
5. ~~IPLV-011, “Measurements of Major Cations in Water Samples by the Flame Atomic Absorption Spectroscopy System.”~~

See DCN #1

6. IPLV-017, “Pipettor Use and Calibration Check.”
7. ~~IPLV-030, “Preconcentration of Rare Earth Elements.”~~

New IPs: IPs for the LA-ICP-TOFMS of minerals will be driven by Scientific Investigation Control, QAP 3.0, until the process becomes stable enough for the IP to be written.

10.0 HOLD POINTS

There are no prerequisites or hold points associated with this work. Decision points associated with the analytical measurements are addressed by use of quality controls to indicate when there is an analytical or other problem which needs action described in the IPLVs.

11.0 QUALITY CONTROL

Precision will be addressed through the analysis of replicates. Accuracy will be evaluated using initial and continuing calibration verifications, and standard reference materials (when available).

12.0 DATA RECORDING, REDUCTION, AND REPORTING

When possible, data packages consisting of the hard copies of raw data generated from each instrument will be referenced by the analysis date and will be attachments to the scientific notebook. Data recording requirements for each scientific notebook are described in the corresponding IPLV. For the ICP-MS results, a summary of data generated from instruments is exported to a spreadsheet (Microsoft Excel) where final data reduction is performed. A hard copy of the spreadsheet containing the reduced data will be included in the data package. If transferred electronically, the data will be zipped to document that there was no data corruption in the process. The final verified reduced data for submittal to the TDA will be controlled in accordance with QAP-3.1. If data is obtained that is unqualified, it will be used for corroboration only and no conclusions will rely solely on that data.

13.0 REVIEWS AND VERIFICATIONS

Internal verification of all data will be performed by someone other that the originator to check compliance to the procedures and to verify the accuracy of the data reduction. Internal technical review will be performed and documented on the data, scientific notebooks, all reports, and journal articles (non-deliverables) generated in this task. In addition, QA review will be conducted on plans, procedures, data, scientific notebooks, and qualified reports. Any report of data generated without full internal verification will be labeled as “preliminary” data. Data review and verification will include the following: check for compliance with criteria described in each procedure and visual inspection and comparison of the data to be submitted to the TDA to that of the reduced data to ensure accuracy. Data will be acceptable when the data review and verification steps are successfully completed.

14.0 RECORDS AND DELIVERABLES

QA records are handled in accordance with QAP 17.0, “Quality Assurance Records.” Records designated as QA records in the UCCSN QAPs and IPLVs listed include but are not limited to:

1) Hard copies and/or electronic media containing raw and reduced data including calibration and QC results.
2) Scientific Notebooks including attachments.
3) Calibration and checks for each balance and pipettor used to collect or produce quality affecting data for this study.
4) Chain of custody forms.
5) Copies of quality affecting deliverables.

In-house records will be protected in the following manner. Records will be stored in a 1-hour rated fire proof safe in locked laboratories. Copies of records will be made and provided to QA personnel on a periodic basis. Electronic data will be stored on the HRC server, which is backed up on a nightly basis. Any data transferred electronically will be checked to verify that was no corruption during the transfer.

Qualified reduced data used in technical reports will be submitted to the Technical Data Archive (TDA) in accordance with QAP 3.6, "Submittal of Data to the Technical Data Management System".

Submittals will be reviewed and signed by the UNLV Research Foundation prior to delivery to the DOE. These include but are not limited to:

1) Qualified final technical report
2) Quarterly Progress Reports