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Determining the Redox Properties of Yucca Mountain-Related Groundwater Using Trace Element Speciation for Predicting the Mobility of Nuclear Waste

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Nevada System of Higher Education (NSHE)

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SCIENTIFIC INVESTIGATION PLAN (SIP)

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Principal Investigator date
James Cizdziel

[redacted] 2-14-06

QA Manager date
Amy Smiecinski

REVISION HISTORY

Revision Number	Effective Date	Description and Reason for Change
0	2/14/2006	Initial issue.

1.0 Scope and Objectives

The objective of this task is to determine the principal oxidation state (redox) species of select elements in samples of groundwater in the vicinity of Yucca Mountain (YM), which is being evaluated as a site for geologic storage of the nation's spent nuclear fuel and high-level nuclear waste. Samples to be analyzed include, but are not limited to, groundwater from wells of the Nye County Early Warning Drilling Program. Elements to be studied include arsenic (As), antimony (Sb), selenium (Se), chromium (Cr), manganese (Mn), iron (Fe), copper (Cu), molybdenum (Mo), vanadium (V), tungsten (W), rhenium (Re), and uranium (U). The purpose is to develop a more accurate and complete description of the redox properties of YM-related groundwater, which influences the solubility and consequently the transport of radionuclides. Indeed, a possible natural barrier to radionuclide migration in the saturated zone (SZ) is the presence of non-oxidizing or reducing environments. For example, the mobility of Tc-99 in oxic groundwater, ascribed to the pertechnetate ion, is greatly diminished in reducing groundwater. The containment of radionuclides away from the accessible environment is a key feature in the Yucca Mountain performance assessment.

Note: This SIP stems from a proposal for a two year project with the same title. Currently the project is funded only for the first year and consequently this SIP reflects work to be conducted during that period. A new SIP will be prepared upon securing funding for the second half of the project. This work is subject to the Nevada System of Higher Education (NSHE) Quality Assurance (QA) program requirements.

2.0 APPROACH

The details of each experiment, including sampling and analytical procedures, will be detailed in the scientific notebook or implementing procedure(s) (IP) depending on the frequency of the experiment/procedure. The general approach to sample collection and the redox measurements are summarized here. We will use results from a previous investigation to guide our collection and analysis scheme (Task 33, Cooperative Agreement No. DE-FC08-98NV12081). The project evaluated various sample preservation techniques and developed ion chromatography (IC) inductively coupled plasma mass spectrometry (ICPMS) procedures for the measurement of oxidation states of most of the elements of interest in this study. Details of the project can be found in the final report (#TR-03-012) on the NSHE Quality Assurance Program website (http://hrc.nevada.edu/QA/Report/TR-03-012.pdf).

Groundwater samples are expected to be collected in collaboration with the Nye County Nuclear Waste Repository Project Office (NWRPO) for wells of the NCEWDP. Other opportunistic samples outside this network may also be obtained. We will attempt to collect samples in a manner to preserve their native state so that the element species remain unchanged from those of the actual, in-situ groundwater. For example, when feasible we will use nitrogen rather than air to pump the wells. Samples may also be collected under an inert atmosphere (such as argon) and/or flash frozen to "lock-in" redox conditions. Elements particularly prone to redox changes with time, such as Cr, will be analyzed as soon as possible, often within hours of collection. These and other approaches will be evaluated to determine the best and most practical method for collecting and preserving the samples.

Samples will be directly injected into the IC and carried through the analytical column by a liquid eluent. An anion or cation exchange column separates the various redox species based on their affinity for the column resin. Species that do not interact with the column resin elute first, whereas those that strongly interact with the column resin elute later. The liquid effluent from the column is introduced to a nebulizer where a stream of argon gas converts it into a fine aerosol. The aerosol or dry particles (if a desolvator is used) are injected into the ICP torch region where ions are produced. The ion beam then enters the mass spectrometer where ions are separated based on their mass-to-charge ratios. The resultant data will be evaluated using graphical and statistical methods to determine the concentrations of the principal redox states and subsequently the redox potential of the groundwaters. Total concentrations of the analytes are expected to be determined as part of Project Activity ORD-FY04-010 (Task 10, Cooperative Agreement DE-FC28-04RW12232). If there is a significant difference between the sum of the concentrations of the redox species and the total concentration of an element, an effort will be made to identify the chemical form of the remainder. For example, if the total concentration of arsenic exceeds the sum of the As^{+5} plus As^{+3}, the remainder may exist in solution as a colloid, such as elemental arsenic As^{o}, or possibly in some organometallic form. Moreover, a fraction of the samples may be analyzed by hydride generation-ICPMS to determine the degree to which the two analytical approaches agree.

3.0 QUALITY ASSURANCE

Prior to the start of quality affecting work, task personnel will undergo QA indoctrination and training. Samples will be collected in accordance with QAP-8.1. Precision will be addressed through the use of field and laboratory duplicates. Precision will vary depending in part on the concentration of the analyte. Accuracy will be evaluated using initial calibration verifications. For the IC-ICPMS, the calibration curve will be checked with a standard from an external source. National Institute for Standards and Technology (NIST) traceable standards will be used (when available) as calibration and check standards. All standards must be accepted by the NSHE QA Program before they are used for quality affecting work (QAP-12.0 4.4.1 describes what must be done to accept unqualified standards). Analytical instruments will be calibrated before each use (where applicable). Our precision and accuracy objectives are to obtain relative percent differences (RPD) for duplicates and recoveries from standards of <25% for elements in the ppb range (1 ppb – 999 ppb), <50% for the ppt range (1 ppt – 999 ppt), and <100% for the ppq range (1 ppq – 999 ppq).

Balances and pipettes will be calibrated at least annually in accordance with QAP-12.0. Calibration items and services will be procured in accordance with QAP-7.0. Lot numbers and manufacturers of analytical standards will be documented or referenced in the scientific notebook. 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. All Measurement and Test Equipment (MT&E) will be protected by storage in a locked laboratory or cabinet to prevent loss and tampering. When NIST-traceable oxidation state standards are not available for calibration or check standards, the basis for acceptance will be documented in the scientific notebook. The skills of task personnel will be outlined in their position descriptions. There is no special training requirements beyond the experience and education listed in the position description. We do not expect to have any subcontracts on this task.

4.0 SCHEDULE OF WORK

Sample collection from NCEWDP wells is dependent on Nye County. In general wells are sampled biannually. We expect some wells to be pumped during the spring and fall of 2006. We may also collect other opportunistic samples depending on time and availability. The laboratory will be prepared, standards and supplies will be purchased and the method revisited. We will perform scoping studies to test procedures and optimize experimental parameters. At the end of this phase be ready to begin experiments with groundwater samples. The samples will also be examined for any “missing” species (difference between the species results and the total result). We will then compile and interpret the data and prepare a final report.

Although sampling of wells is dependent upon Nye County, it is useful to have specific targeted deadlines for the purposes of planning. To that end, data collection should be completed by 7/31/06, data submittals to the Technical Data Archive (TDA) should be completed by 8/31/06, and a report should be approved and submitted to LBL on or before 9/31/06. Note: during the second year of the project (if funded) we continue the sampling and analysis, increasing data coverage, generate a map of redox conditions and predict the solubility and mobility of key radionuclides.

5.0 INTERFACE CONTROLS

External Interfaces:
NCEWDP sampling coordinator: Nye County Waste Repository Office
Lawrence Berkeley Laboratory (Director, Natural Barrier Thrust Area): Gudmundur Bodvarsson
Internal Interfaces:
Principal Investigator: James Cizdziel
Co-PI: Vern Hodge
Co-PI: Karen Johannesson
Analysts: To be determined
Students: To be determined

6.0 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.

7.0 IMPLEMENTING PROCEDURES

The following is a list of IPLVs that may be used in this study:

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-017, "Pipettor Use and Calibration Check."
6. IPLV-039, "IC-ICPMS determination of inorganic arsenic, chromium, molybdenum, tungsten, manganese, copper, selenium, antimony, vanadium and uranium species in groundwater".

8.0 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.

9.0 DATA RECORDING, REDUCTION, AND REPORTING

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. In general, raw data will be reduced to percentages of major redox species and total concentrations based on calibration curves. This data will tabulated and graphed in Microsoft Excel. 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.

10.0 REVIEWS AND VERIFICATIONS

Internal verification of all data will be performed by someone other than 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-submittals) 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. This section does not provide a complete list of criteria for reviews and verifications. More detailed descriptions can be found in QAP-3.0 and the respective IPs.

11.0 RECORDS AND SUBMITTALS

QA records are handled in accordance with QAP 17.0, "Quality Assurance Records." Records designated as QA records in the NSHE 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 submittals.

In-house records will be protected in the following manner. Records will be stored in a 1-hour fire-rated 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 to LBL include but are not limited to:

1) Qualified final technical report
2) Quarterly Progress Reports