Office of
Science and Technology and International

Natural Barriers Targeted Thrust FY 2005 New Start Projects

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PREFACE

This booklet contains project descriptions of work to be performed by the Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRWM), Office of Science and Technology and International's (OST&I) Natural Barriers Targeted Thrust as part of Fiscal Year 2005 new starts. The Natural Barriers Targeted Thrust is part of OST&I's Science and Technology Program, which supports the OCRWM mission to manage and dispose of high-level radioactive waste and spent nuclear fuel in a manner that protects health, safety, and the environment; enhances national and energy security; and merits public confidence. In general, the projects described will continue beyond FY 2005, assuming that the technical work remains relevant to the proposed Yucca Mountain Repository and sufficient funding is made available to the Science and Technology Program.

Project Title	Improved and Stand-Alone Thermal-Hydrological-Chemical Process Model for the In-Drift Chemical Environment
OCRWM S&T Program Thrust	Natural Barriers
Project Performers	Lawrence Berkeley National Laboratory
Principal Investigators	Jens Birkholzer, Carl Steefel, Eric Sonnenthal, Nic Spycher
FY 2005 Funding	$300,000

Abstract **BACKGROUND:** The in-drift chemical environment plays a key role in determining the potential extent of waste package corrosion. Although the Alloy 22 proposed for use in the waste packages has been shown to resist corrosion in most environments, some concentrated solutions that could contact the waste packages can accelerate corrosion, especially those containing the halides Cl^-, F^-, and Br^-. It is therefore critical to establish whether such concentrated solutions or brines will contact the waste package, and if so, in what volumes, for how long, and at what temperatures. Processes that could cause brines to contact the waste package include seepage of water into the drift from above, wicking of water into the invert below the waste package, and deliquescence of salts accumulated on the waste package. Also of concern is the possibility that heating of salt brines in the drift could generate acid gases that might have a corrosive effect on the engineered barrier system (the waste package and the drip shield). In addition, it is necessary to predict how such brines will evolve over time inside the drifts, whether as a result of ongoing transformations within the aqueous phase, exchange with the gas phase, or as a result of liquid or gas transport.

All of these questions are addressed currently with a decoupled numerical approach. First, a thermal-hydrological-chemical (THC) model for coupled processes taking place in the rock surrounding the drift provides the seepage water chemistry and gas composition as a function of location around the drift over time. The output of this model provides the boundary conditions for an in-drift thermochemical reaction-path model with no explicit treatment of either liquid or gas transport. Although the current in-drift chemistry approach incorporates a Pitzer-type database for calculation of solute activities at high ionic strength, the lack of treatment of transport limits its ability to address questions concerning the in-drift chemical environment and its potential impact on engineered barrier system corrosion. Hence the current project approach is fit for its intended purpose of obtaining a license for repository construction, but can be improved upon by adding several capabilities to the modeling, such as: explicit consideration of masses of water and dissolved chemical species that can seep into the drift and contact the waste package, treatment of water vapor and gas transport within the drift, and consideration of how this might be affected by near-field conditions in the rock.

This project involves the development of a fully coupled THC model, in which heat, water, and solute transport are combined with a rigorous thermodynamic approach applicable to highly concentrated brines at variable water activities. This approach will significantly increase the transparency and defensibility of the treatment of in-drift chemical processes. This, in turn, will greatly increase the confidence with which the range of chemical conditions likely to be encountered in the drift can be described, and the corrosive potential of the engineered barrier

system can be assessed.

OBJECTIVES: The objective of this project is to develop a fully coupled THC model that spans the artificial boundaries between the near field rock and drift environments, and to:

1. Couple heat, water, and solute transport in both the drift and near-field environments with a rigorous thermodynamic framework, based on the Pitzer approach that describes the multiphase (liquid and gas) equilibria of concentrated salt brines, and
2. Couple water and gas transport within the drift environment, as affected by the local temperature and relative humidity regime, and to verify that the coupled approach provides an improved description of in-drift chemical processes by comparing simulation results with completed and ongoing experiments (TGA and evaporation) at Lawrence Livermore National Laboratory.

APPROACH: Development of the fully coupled model includes the following tasks:

Task 1: Incorporate Pitzer formulation and existing YMP Pitzer database into THC (Toughreact) model. This task builds on a considerable body of work already completed in which a Pitzer-based thermodynamic database has been developed and a Pitzer formulation has been incorporated into the reaction path code EQ3/6.

Task 2: Validate the Pitzer-based THC model using Thermogravimetric Analysis (TGA) and evaporation experiments conducted at Lawrence Livermore Laboratory. This task will provide the principal validation of the newly developed model. The evaporation experiments will be used to ensure that the Pitzer-THC model is capable of describing solution chemistries over a range of solute concentrations, water activities, and temperature. The TGA experiments will be used to validate both the chemical model in the context of transport, since these experiments were conducted under open (flow-through) conditions.

Task 3: Improve treatment of in-drift gas and water vapor transport using effective parameters derived from computational fluid dynamics (CFD) modeling. The results of CFD modeling at Sandia National Laboratories will be used to provide effective binary gas diffusion coefficients that describe gas dispersion in the drift environment. Although not the primary focus on this research project, such a capability is essential for addressing the problems of water and gas transport and the fate of any acid gases generated.

Task 4: Simulate with the Pitzer-THC model the seepage of water into the drift from above and the wicking of water into the invert from below, tracking the time and spatial evolution of the solution and gas chemistry. Along with Task 5, this will provide the principal results that can be used to improve the understanding of the in-drift chemical environment, adding both transparency and scientific defensibility to conclusions about the in-drift chemical environment and its impact on waste package corrosion.

Task 5: Simulate the generation and transport of acid gas due to volatilization from salt brines in the drift environment. This task will specifically focus on the problem of acid gases that may be generated by heating of saline brines in the drift. A range of salt compositions will be examined, with gas fugacities constrained by the high ionic strength Pitzer model. Both water and heat transport will be combined with the gas transport to provide a realistic description of the transport and fate of acid gases in the two and three dimensional drift environment. Axial transport of gases and water down the length of a drift containing waste packages with differing temperatures will also be considered. Finally, the effects of the drip shield will also be explicitly evaluated.

Task 6: Simulate feedback of corrosion products on in-drift chemical environment. Tasks 4 and 5 simulations will include the feedback of corrosion products (e.g., Fe-oxides) as determined by the corrosion studies and modeling performed at Case Western University and Lawrence Livermore National Lab. This task will assess any impacts of these corrosion products on in-drift gas fugacities (in particular oxygen), aqueous species transport, and their role in modifying the in-drift chemical environment.

Project Title	Integrated Assessment of Critical Chemical and Mechanical Processes Affecting Drift Performance: Laboratory and Modeling Studies
OCRWM S&T Program Thrust	Natural Barriers
Project Performers	Penn State University, Lawrence Berkeley National Laboratory
Principal Investigators	Derek Elsworth, Jonny Rutqvist, Abraham Grader, Chris Marone, Eric Sonnenthal
FY 2004 Funding	$400,000

Abstract **BACKGROUND:** The importance of the interaction between stress, temperature, chemistry, and hydrology in controlling the performance of a deep geological repository for nuclear wastes has been apparent for at least two decades. To date, performance evaluation, and the supporting science, has largely developed along two separate lines: one focusing on the role of hydrothermal effects mediated by chemistry (THC), but absent direct mechanical influences; and one focusing on the role of mechanical effects in mediating the hydrology (THM), but absent the direct influence of chemistry. This separation is justified where there is no clear linkage of stresses mediating chemical effects, and conversely of chemical potentials mediating mechanical behavior.

However, recent data identify the profound influence of stresses on the transport characteristics of fractures, driven by chemistry alone. These coupled mechanical-chemical effects show permeability reduction of over two orders of magnitude occurring under modest temperatures (~20°–150°C) and stresses (~3 MPa), and over the period of only a few weeks. These observations are important because: (1) they are counterintuitive—permeability reduces with net dissolution; (2) they occur under conditions anticipated to endure over substantial periods in the drift-local environment; (3) the effects are of large magnitude.

This project will provide constitutive data for the mechanical and transport properties of fractures in relevant repository units of Yucca Mountain Topopah Spring welded tuff (TSw2 thermal-mechanical unit including Tptpmn and Tptpll lithostratigraphic units) as a result of hydrothermal alteration. These constitutive relations will be used in forward models for strongly-coupled thermal-hydrological-mechanical (THM) and thermal-hydrological-chemical (THC) response, to be developed in this work, which will include the representation of fluid transport and drift-degradation through ultimate collapse. Uniquely, these models will identify interactions between stress and chemistry that have been shown to induce reductions in permeability of several orders-of-magnitude, under anticipated drift-local temperatures (~140°C) and stresses (~5–30 MPa), and are anticipated to have an important influence on drift response.

OBJECTIVES: This study offers the potential to (*1) significantly improve understanding of near-field processes*, by means of unusually well-constrained laboratory data to define changes in the mechanical and transport properties of

fractures as a result of hydrothermal conditions anticipated in the drift-local environment. These new data will *(2) improve realism in performance calculations*, by enabling accurate modeling of the evolving paths of temperature, stress, fluid saturation, and chemical potential, anticipated in the drift environment, including the effects of strong process-couplings and the representation of post-collapse response. *This approach is (3) novel as it will* supply unique experimental data, not currently accommodated in performance assessment**,** that will be utilized in state-of-the-art modeling tools to define long-term performance of the drift.

APPROACH: The novelty of this study is both in the experimental methods, providing unusual constraint on heretofore absent couplings in physical response—and in the application of numerical modeling, proposing linkages between uniquely qualified codes to extend laboratory observations to field-scale.

The selected experimental methods provide unusual constraint on processes at prescribed *in situ* hydrothermal and stress conditions:

• Flow-through reactor experiments are monitored for the evolution of porosity and permeability with three signals—direct measurement of permeability, mineral mass efflux, and noninvasive x-ray CT images.

• Double direct shear experiments define the failure response of natural fractures, with concurrent evaluation of permeability and capillary characteristics, and the measurement of mineral mass efflux.

• Together, these experimental constraints provide unequivocal definition of active processes at the microscale, and enable extension to macroscale behavior. These behaviors, at high stresses and temperatures, and for potential repository units, are currently undefined.

The modeling approach offers the potential to rigorously incorporate these unique behaviors, for the first time:

• The rigorous coupling between THM and THC effects will allow appropriate paths of stress, temperature, saturation, and chemical potential to be followed. This coupling is important where stress has an important effect on chemistry, *via* pressure solution—a key tenet in this proposed study.

• The proposed coupling of the hydrothermal-chemical code TOUGHREACT (THC) with the mechanical code FLAC3D (THM) is a novel extension of state-of-the-art capabilities, proven feasible and achievable by the coupling of the hydrothermal and mechanical codes TOUGHFLAC.

• The proposed coupling of TOUGHREACT (THC) with 3DEC (THM) is a novel extension of these capabilities, to allow large deformations and drift collapse to be followed in time, again constrained by the unique constitutive data to be developed in this study.

Project Title	Thermal Hydrological Near-Field Model Studies and Impact of Natural Convection on Seepage
OCRWM S&T Program Thrust	Natural Barriers
Project Performers	University of Nevada, Reno; Lawrence Berkeley National Laboratory
Principal Investigators	George Danko, Jens Birkholzer
FY 2005 Funding	$255,000

Abstract **BACKGROUND:** The main concept of this project is that differences and variations in temperature and moisture distributions in the near-field rock mass can be made major assets in waste containment, provided that they can be modeled, understood, and engineered. The in-drift moisture transport along the drift length, as well as the condensate trapping process, will be modeled and harnessed for moving water away from the waste packages, forming a robust barrier for several thousands of years. Instead of fighting the negative effects of local variations and condensate trapping, they will be modeled, understood, used, and engineered, as a new science and technology concept.

OBJECTIVES: The goal of this project is to acquire an improved understanding of the coupled in-rock and in-drift processes. Innovative numerical modeling capabilities would be developed to describe the coupled in-rock and in-drift processes (such as seepage, condensation, and in-drift ventilation) for an assumed waste package arrangement conducive to effective barriers for drift seepage.

APPROACH: An integrated scientific-engineering-mathematical modeling method and numerical model will be used to solve the coupled near-field and in-drift thermal, hydrological, natural air movement, and condensation processes. The coupled in-rock and in-drift transport processes will be modeled using numerical codes MULTIFLUX (MF) with (1) TOUGH2 for the in-rock processes both above and below the drift in the unsaturated zone; (2) a lumped-parameter code CFD4 for the in-drift transport processes, including natural air convection and condensation around the waste packages; and (3) an iterative coupler for enforcing boundary coupling of the heat and moisture transport processes on the interface between the drift air space and the rock mass surrounding the drift. MF applies an innovative surrogate-model element, obtained from a Numerical Transport Code Functionalization (NTCF) procedure, reducing the number of TOUGH2 runs during iteration. Support simulation results for in-drift air-flow calculation will be imported from a commercial CFD code, such as FLUENT and incorporated into the coupled solution.

The key elements in the project approach are as follows:
1. An updated numerical model, with the most recent hydrological properties, will be formulated that captures all key elements of the near-field thermal, hydrological and passive transport processes coupled to the processes in the emplacement drift. The model will have the fine scale and finesse to give detailed information in 3D about the near-field variations in temperatures and concentrations. At the same time, the model will describe at least an entire emplacement drift as a minimum representative volume

(MRV). In the MRV, the in-drift transport processes provide an effective axial connection between the hot and cold sections.

2. The numerical MF model will be tested and validated against the Drift Scale Test field results. The hypothesis is that, similarly for previous validation tests, the model will pass, providing partial compliance with quality control requirements as well as confidence in further applications. The MF4.0 software would be qualified.

Project Title	Literature Survey of SZ plumes in Volcanic Rock
OCRWM S&T Program Thrust	Natural Barriers
Project Performers	Los Alamos National Laboratory, United States Geological Survey
Principal Investigators	
FY 2005 Funding	$300,000

Abstract **BACKGROUND**: In the current Yucca Mountain saturated zone models, radionuclide plumes are predicted to have a relatively narrow shape. The very narrow plumes limit the opportunity for radionuclide transport to be retarded through sorption. The small lateral dispersion exhibited by these plumes may be relatively unusual compared to dispersion observed with chemical plumes at other sites in similar geologic settings. This study proposes a systematic investigation of transport plumes in volcanic rock.

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OBJECTIVES: The objective of this work is to allow OST&I to determine if there is sufficient evidence to support a substantial effort in characterizing potential plume geometry, in order to constrain the prediction of future Yucca Mountain repository plumes with greater confidence

APPROACH: This project involves conducting a literature survey of occurrences of radionuclide plumes in saturated, fractured volcanic rocks worldwide, to determine the common characteristics of plume geometry and controlling hydrological parameters. The survey will focus on fractured, volcanic rock and will emphasize systems similar to Yucca Mountain (such as the Nevada Test Site), but will include insights from other types of fractured, layered rock as well. The goal is to begin with a broad literature search and then narrow the search to those sites with the most information for more detailed study. Sites identified during the literature survey that are well characterized, with sufficient supporting data, will be the focus of more in-depth analysis and interpretation. The survey will encompass a variety of types of plumes, including natural chemical/isotopic plumes, contaminant plumes, and plumes generated by controlled tracer tests.

This study will attempt to characterize the whole dispersive/diffusive process, including concepts such as channeling, subgridblock diffusive transport, and other mechanisms that influence dispersion and diffusion. Specificity of hydrological parameters, such as transverse-horizontal and transverse-vertical dispersivity, will be one part of this characterization. If deemed appropriate, models will be constructed to simulate various dispersion and diffusion mechanisms.

A final report will be submitted to OST&I by September 30, 2005. This report will provide conclusions and recommendations for further studies that include modeling and characterization of saturated zone transport at Yucca Mountain. It is also anticipated that the results of this study will lead to one or more journal articles in peer-reviewed literature.

Project Title	Field Studies for the Determination of Transport Properties of Radioactive Solutes and Colloids, Using Chemical Analogues
OCRWM S&T Program Thrust	Natural Barriers
Project Performers	Lawrence Berkeley National Laboratory, Los Alamos National Laboratory, Nye County Nuclear Waste Repository Project Office
Principal Investigators	Barry Freifeld, Paul Reimus, Dale Hammermeister, George Moridis, John Apps
FY 2005 Funding	$197,000

Abstract: **BACKGROUND:** While advective transport in the natural system occurs predominantly along fractures, estimates for sorption have typically neglected this because of the great difficulty (with current indirect measuring methods) in quantifying water/rock interaction along the mineral coated fracture surfaces. Neglecting the potentially high sorptive capacity of fracture-coating minerals results in a sorptive model that primarily reflects diffusion into and sorption onto the less reactive rock-matrix materials. Because many of the retardation mechanisms controlling radionuclide transport in the Saturated Zone (SZ) have been difficult to quantify, the conservative assumption has been not to incorporate them into process models. Specifically, the SZ process models do not account for: (1) highly-sorptive mineral surface coatings in primary advective fracture pathways, (2) irreversible sorption or very slow desorption of some solutes, (3) the possibility of reducing redox potentials that could result in precipitation or enhanced sorption of some solutes, and (4) irreversible colloid filtration.

Field injection pump-back tests proposed for this project would quantify rates for radionuclide sorption/desorption and filtration of colloid-borne radionuclides applicable to Yucca Mountain SZ transport. Because of the impracticality of performing field studies using radionuclides of primary importance—uranium (U), neptunium (Np) and technitium (Tc)—reactive chemical analogues would be used. By performing batch reactor tests, using both the chemical analogues employed in the field, along with actual radionuclides, new estimates of sorptive parameters for U, Np, and Tc applicable to field conditions will be derived. Similarly, estimates for filtration and retardation of colloids, currently treated very conservatively in SZ process models, can be obtained from the field tests.

OBJECTIVES: The primary objective of this work is to provide an enhanced understanding of the transport behavior of radionuclides and colloid-bound radionuclides in the SZ, using field measurements conducted with chemical analogues. These measurements will be performed within wellbores penetrating the three major volcanic rock types—devitrified, zeolitic, and vitric—within the SZ. Direct measurement of the retardation processes controlling radionuclide transport in the natural system, using chemical analogues, will facilitate their incorporation into models predicting radionuclide transport through the SZ. Next-generation reactive transport models will be developed that incorporate distributions of sorption, desorption, and colloidal filtration parameters, and recommendations on how these mechanisms could best be incorporated into Yucca Mountain performance assessment models will be made.

APPROACH: Three institutions (LBNL, LANL, NWRPO) will collaborate on this project, in recognition of the operational and scientific complexity of the proposed testing plan. LANL, with its long history of laboratory studies in radionuclide transport, will perform the laboratory studies. LBNL and LANL will work together to interpret reactive transport, using combined staff and numerical tools. LBNL will lead in assessing suitable testing sites using the best understanding of SZ hydrological conditions, as well as detailed information on all of the SZ boreholes.. The NWPRO will supervise site activities and interface with the State of Nevada for permitting of tracers used in the field.

The proposed injection pump-back tests make use of a new geochemical sampling tool and its accompanying sampling methodology, referred to simply as the U-Tube. The U-Tube can acquire large volume fluid samples from deep boreholes at *in situ* conditions, while permitting precise control of the volumes of fluid sampled by means of control valves at the surface. It simplifies the downhole wellbore completion, eliminating the need for deep-well submersible pumps, and improves control on testing boundary conditions. The greatest benefit for performing reactive transport studies with the U-Tube is the high-purity at which the samples are acquired, without depressurization, degassing, or exposure to contaminants (e.g., air).

Existing boreholes will be selected that penetrate the SZ through lithologies representative of the three major volcanic rock types—devitrifield, zeolitic, and vitric. Each borehole will be completed so that multiple transport tests can be run concurrently, with the goal of testing two intervals for each of the three major volcanic rock types. In the planned injection pump-back tests, conservative tracers will be introduced along with chemical analogues, to provide a reference by which to compare with the reactive solutes. The elution of conservative tracers during pump-back provides a means to assess both specific discharge and matrix diffusion in the SZ.

A reactive transport test proceeds as follows: (1) A straddle packer is set to isolate each zone of interest. The zone is completed with a U-Tube sampler and a tracer injection tube. (2) Native fluid is produced with the U-Tube and while still under formation pressure at *in situ* conditions, conservative and reactive tracers are mixed with the fluid. (3) The tracer cocktail is injected into the formation chased by a slug of native fluid. (4) The most important step—wait. (In this phase the tracer will move advectively, diffusively, and will react with the natural system without any injection or pumping.) (5) Pump-back with the U-Tube. The resulting tracer elution curves (evolution of concentration vs. time in the extracted volume) will be analyzed to estimate the parameters that describe the equilibrium or kinetic sorption (or filtration, for colloids) of the tracers. (6) Wait (not as long as Step 4). (7) Pump-back with the U-Tube. Tracer elution curves from this step will be analyzed to provide rate estimates for desorptive processes and to provide more refined estimates of matrix diffusion parameters. Step 6 and Step 7 can be repeated to better understand desorption kinetics.

The analysis of the tracer elution data will involve inverse modeling (history matching) of the concentration of the tracers in the fluid withdrawn from the well. In the proposed analysis approach, inverse modeling will be used to correlate the elution curves with different models of sorption or filtration behavior. The results of the laboratory batch tests on tracer sorption, or filtration and data from previous studies, will provide an indication as to the type of processes occurring under field conditions. Kinetic sorption, equilibrium sorption (linear, Langmuir and Freundlich), and site complexation models will be considered for participating chemical species, unless significant mismatches necessitate fuller model development. Then, inverse modeling will determine the parameters of the sorption/filtration model under consideration by minimizing the discrepancy between measurements and predictions.

To draw meaningful comparisons between the behavior of the radionuclides and their surrogates, a detailed analysis will be performed on the adsorptive chemistry of each surrogate, in the context of the environmental conditions imposed by the local chemistry in the well at the study location. Batch laboratory studies of sorption and desorption of radionuclides and their surrogates will be undertaken to compare their sorptive behaviors. Ion exchange, surface complexation, and co-precipitation of the radioelements and selected surrogates will be assessed. When practical, batch testing will proceed with waters and rock samples from the proposed injection pump-back testing intervals. Natural colloids collected from Nye County wells (known to be primarily smectite clays), as part of other Yucca Mountain studies, will be used for adsorption and desorption testing of radionuclides and surrogates onto colloids. Tests will be conducted over a range of pH and carbonate/bicarbonate concentrations to help elucidate mechanistic similarities and differences between the surrogates and radionuclides. The batch sorption/desorption studies will be supplemented with a limited number of XPS (X-ray photoelectron spectroscopy) comparisons of tuff surfaces (with special emphasis on fracture mineral coatings) that have significant concentrations of radionuclides or surrogates adsorbed to them.

The field tests and laboratory studies will be interpreted using a reactive transport modeling approach that accounts for distributions of sorption and desorption, as well as colloidal filtration. Interpretation of testing results will be correlated with understanding of rock mineralogy and water chemistry to provide fundamental underpinnings for upscaling of results, preliminary to incorporation into predictive SZ transport models.

Project Title	Determining the Redox Properties of Yucca Mountain-Related Groundwater, Using Trace Element Speciation for Predicting the Mobility of Nuclear Waste
OCRWM S&T Program Thrust	Natural Barriers
Project Performers	University of Nevada, Las Vegas; University of Texas, Arlington
Principal Investigators	James Cizdziel, Vernon Hodge, Karen Johannesson
FY 2005 Funding	$300,000

Abstract

BACKGROUND: 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. Despite the significant implications of a potential natural barrier in the SZ, little is known about the true oxidizing/reducing (redox) conditions in the SZ below and downgradient of Yucca Mountain (YM). This is because the traditional measurements of Eh by a platinum electrode may not be a valid indicator of the actual redox conditions. A necessary assumption for the definition of Eh is that the system is in equilibrium—but natural systems are rarely in equilibrium, because equilibration time for many environmentally important reactions is on the order of years to centuries. In addition, most redox couples do not react on a platinum surface at near-neutral pH values, and groundwater samples in southern Nevada typically have pH values that range from 7.2 to 8.2.

This project is based on an approach for determining redox properties other than Eh. The investigators have developed methodology to measure the concentrations of redox-active species of a number of trace elements in groundwaters by the ion chromatography-inductively coupled plasma mass spectrometry (IC-ICPMS) technique. Results from application of the technique to select samples of groundwater collected from Nye County Early Warning Drilling Program (NCEWDP) Wells suggested that there are some groundwater flow paths that may contain reducing conditions favorable to immobilization of radioactive elements.

OBJECTIVES: The proposed research will focus on determining the oxidation state species of ten elements (arsenic, antimony, selenium, chromium, manganese, copper, molybdenum, vanadium, tungsten, and uranium) in samples of NCEWDP groundwater and other available samples beneath and downgradient from the YM Repository. Additionally, the IC-ICPMS method will be developed for speciating iron and rhenium. Percentages of major redox species of these elements and total concentrations will be measured and tabulated. The objective is to obtain information that is accurate and that provides a more complete description of the redox properties of YM-related groundwater. A three dimensional “map” of redox-condition distributions in the aquifer will be built, to subsequently be overlaid with regional groundwater flow models. The purpose is to predict likely zones within

the flow system where changing redox conditions could lead to sequestering of potentially dangerous radionuclides.

APPROACH: This project would apply the trace element speciation approach to provide a more accurate picture of the redox conditions of groundwater in the vicinity of YM, to help determine whether a natural reducing barrier exists, and if such a barrier is identified, to establish its magnitude and spatial distribution. The redox information will be interpreted to shed light on the solubilities and mobilities of key radionuclides in the SZ environment.

Specifically, the project would build on the IC-ICPMS technique to (1) further examine groundwater sample collection and preservation techniques that "lock in" the redox species present in the groundwater prior to sampling; (2) add important elements such as iron, whose geochemistry may play a role in radionuclide transport, and rhenium, a surrogate for technetium- 99; and (3) expand sample collection and corresponding data coverage.

The results could be used to predict whether an element not measured—such as plutonium, neptunium or technetium—would be likely to exist in reduced or oxidized forms. The information would facilitate predictions of the mobility of an element based on the dominant species' solubility or affinity for solid surfaces.

The approach would be based on measurements of the redox species at realistic, trace concentrations. It will improve the understanding of the SZ environment downgradient of YM, which may, in turn, lead to a more accurate and less conservative model.