Uranium Recovery Research Sponsored by the Nuclear Regulatory Commission at Pacific Northwest Laboratory

Quarterly Progress Report, June - September 1983

November 1983

**Prepared for the U.S. Nuclear Regulatory Commission
under Contract DE-AC06-76RLO 1830
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**Pacific Northwest Laboratory
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

URANIUM RECOVERY RESEARCH
SPONSORED BY THE NUCLEAR
REGULATORY COMMISSION AT
PACIFIC NORTHWEST LABORATORY

QUARTERLY PROGRESS REPORT
JUNE TO SEPTEMBER 1983

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Pacific Northwest Laboratory
Richland, Washington 99352

EXECUTIVE SUMMARY

This report documents progress for four major research projects which include 9 discrete research tasks and a management task being conducted for the U.S. Nuclear Regulatory Commission (N.R.C.), Office of Research, Waste Management Branch. The primary purpose of these tasks is to provide information to help the NRC license uranium recovery facilities. A truncated title of each task and a brief highlight summary are provided here.

- Long-Term Stabilization

Hydrologic modeling of the Grand Junction study site was completed, the extent and velocity of flood impingement on the UMT pile determined, and design of the riprap completed. Field work (surveying) was completed for the Slickrock study site, and the 2 ft contour topographic maps of the Dolores River affecting the UMT pile received from the subcontractor.

The literature reviews for riprap design for overland erosion and local scour by flood flow were completed, and the ones for riprap design for local drainage channels and impoundment slope stability started.

The first draft of the report on vegetative covers was completed, and the vegetative cover test plots were sampled after their second growing season.

Economic evaluations of alternative riprap designs were underway for the Grand Junction study site using inputs from the hydrologic modeling and from field work conducted in June on sources of rock near the Grand Junction and Slickrock sites and their relative durabilities and resistances to weathering.

- Interim Stabilization of Mill Tailings Piles

A plan for field-testing commercially-available windscreens and additional chemical stabilizers was developed, and field tests initiated. A report of the 1982 field tests of chemical stabilizers was completed.

- Tailings Dewatering Techniques

The consolidation theory that is available in the variably-saturated flow and consolidation model TRUST has been determined to be inadequate for the analysis of hydraulically-filled tailings pits. A more recent theory developed by Fredlund and Morgenstern has been shown to be the better description. This new theory which is based on a two stress-state description of the void ratio, saturation and hydraulic conductivity in the partially-saturated zone has been incorporated into the model algorithm (now called TRUST-II). Classical consolidation theory will still be used in the saturated zone. Testing of the model solutions with and without consolidation has been completed for the saturated regime. Testing of the partially saturated consolidation results will be finished as soon as data from the Grand Junction slimes are obtained.

The apparatus necessary for obtaining soil properties has been installed and modified to perform the necessary laboratory measurements. Initial testing has been completed and measurements of mill tailings slimes has begun. In addition, methods for preparing input to TRUST-II and for analyzing the results have been developed and reported. This package of routines contains several computer programs for preparing soil characteristic data, for developing numerical grids, and for analyzing the transport of contaminants through the flow field generated by TRUST-II.

- Tailings Neutralization and Other Alternatives in Immobilizing Toxic Materials in Tailings

Initial results with neutralizing barriers (compacted on-site sediments add-mixed with lime and used as part of a tailings pit liner) show dramatic decreases in permeability as contact with acidic tailings solution continues. This type of solution treatment, in which only the portion that escapes is treated, has the advantages of allowing recycling of acidic solutions and reducing capital equipment expenditures and operating costs in comparison with other neutralization schemes. Analysis of collected effluent solutions to measure reduction in the amount of contaminants escaping is in progress as are leach tests on neutralized tailings.

Funding for this task in Uranium Recovery was eliminated for FY-84; however, additional FY-83 funds were obtained to complete some important parts of the work.

- Disposal Techniques Allowing Contact with Ground Water

Significant progress has been made on a method to evaluate the environmental consequences of disposing uranium mill tailings in deep mine stopes below the water table. The approach reduces data-input requirements and concentrates on considerations of the permeability contrasts between the tailings in the mine stope and the surrounding medium, and on the orientation of the stope relative to the local ground-water flow field. Chemical interactions will be included in the analyses, pending the outcome of coupled transport and chemical modeling to be done in FY-84.

- Effluent and Environmental Monitoring Methods and Equipment and Instrument Testing

Field comparisons of short-term and long-term radon and radon-daughter measurements have been integrated in order to maximize results from the remaining funds for this task. An occupied and a vacant house in Edgemont, South Dakota, have been instrumented, and data are being transmitted to PNL for analysis. Laboratory evaluation of selected methods for analyzing yellowcake continued, as did that for methods of measuring 226-Ra, 230-Th, and 210-Pb. Field testing of well-logging techniques was completed, and the PNL calibration facility was cross-calibrated with that of the Grand Junction Technical Measurements Center. A topical report recommending sampling strategies for

temporal and spatial evaluation of contaminants was completed, and a data set was selected to test several ground-water sampling strategies. A hundred radon flux measurements were made in Edgemont, South Dakota, for comparison with 226-Ra concentrations in surface and subsurface soils. Funding for this task in Uranium Recovery was eliminated for FY-84.

- Attenuation of Radon Emissions

Topical reports assessing the influence of defects on radon diffusion and describing advective transport in cover soils were completed and sent to NRC. A handbook for determining radon attenuation through cover soils was completed and is in peer review, as was a draft of a document in regulatory guide format describing the determination of radon attenuation by cover soils.

- Assessment of Leachate Movement

A topical report describing predicting geochemical modeling of interactions between tailings solutions and sediments was completed and sent to NRC. Column experiments, including ones designed to measure scale effects, were completed and predictive geochemical modeling of column experiments was compared with experimental results. Field work to obtain data related to seepage from a tailings pond was completed, and the geochemical modeling will be compared against actual field data.

Funding for this task in Uranium Recovery was eliminated for FY-84; however, the work is applicable to other waste forms and will be funded at a reduced level in FY-84 in Low-Level Waste.

- Methods of Minimizing Ground-Water Contamination in In-Situ Leach Uranium Mining

Sediment samples have been collected from a Wyoming roll-front uranium deposit. The sediments will be used to characterize the geochemistry of a typical Wyoming deposit and to determine differences and similarities between the Wyoming chemical environment and that of the Texas site sampled last year. Also, the sediments will be used in laboratory experiments to evaluate restoration methods.

A batch experiment with the Texas aquifer sediments and lixiviant was completed this quarter. It showed that undisturbed contact of the solution and sediment can lead to a series of reactions that might temporarily increase iron concentrations in solution to above baseline levels, but will ultimately lower the redox potential of the solution leading to low dissolved iron and uranium concentrations.

Theoretical calculations showed that sulfur-bearing reductants will effectively lower oxygen concentration in spent lixiviant and will decrease the redox potential to the point that uranium and other redox-sensitive contaminants will be removed from solution by mineral precipitation. Sulfide will also combine with any ferrous iron released during the process of reducing the aquifer to form relatively insoluble minerals that will limit the dissolved iron concentration to below contaminant levels.

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INTRODUCTION

Pacific Northwest Laboratory (PNL) is currently conducting research for the U.S. Nuclear Regulatory Commission (NRC) on uranium recovery process wastes for both active and inactive operations. The overall objective of this research is to provide NRC and their licensees with technical guidance on several issues related to management of wastes from uranium mills and in situ recovery operations. Principal issues addressed in these studies are: designs and performance of radon-suppression covers; the incentives and constraints for using protective covers, and designs for armoring tailings pile radon-suppression covers; short-term stabilization options for controlling windblown particles; leachate movement in soil; tailings dewatering and consolidation; disposal deliberately below the water table; neutralization incentives; contamination control and restoration in in situ uranium recovery; and environmental measurements, instrumentation, and protocols for assessing the radioactive contamination associated with uranium milling and mill tailings. Results of these studies will provide means to better evaluate the environmental impacts during and following the active life of a uranium recovery facility, and many will be used in developing regulatory guides.

The National Research Council Committee on Onshore Energy Minerals Management Research (COEMMR) stated:

"The most significant unresolved (uranium) milling-related problem appears to be the safe disposal of radioactive and heavy metal-laden mill wastes. Potentially suitable tailings management techniques, using different approaches, have been adopted at several of the mills commissioned in the last few years. It is important that field performance of both old and new techniques be monitored and the data critically examined to determine the effectiveness of the different methods, and the nature of any required modifications."

NRC-sponsored uranium recovery research at PNL is focused on NRC regulatory responsibilities for uranium-recovery operations:

- license active milling and in situ extraction operations,
- concur on the acceptability of DOE remedial-action plans for inactive sites,
- license DOE to main inactive sites following remedial actions

(a) Information available in Proceedings of the Workshop on Research and Information Needs for Management of Uranium Production from Leased Federal and Indian Land, held December 9-10, 1982, Albuquerque, New Mexico. In publication through the Committee on Onshore Energy Mineral Management Research sponsored by the National Research Council, Washington, D. C.

PNL's program consists of four coordinated projects comprised of a program management task and nine research tasks that address the critical technical and safety issues for uranium recovery. Specifically, the projects endeavor to find and evaluate methods to:

- prevent erosion of tailings piles and prevent radon release from tailings piles
- evaluate the effectiveness of interim stabilization techniques to prevent wind erosion and transport of dry tailings from active piles
- estimate the dewatering and consolidation behavior of slurried tailings to promote early cover placement
- design a cover-protection system to prevent erosion of the cover by expected environmental stresses
- reduce seepage into ground water and prevent ground-water degradation
- control solution movement and reaction with groundwater in in situ extraction operations
- evaluate natural and induced restoration of groundwater in in situ extraction operations
- monitor releases to the environment from uranium recovery facilities.

This quarterly progress report for the uranium recovery research program at PNL covers the research performed for the NRC at PNL in the period June, 1983 through September, 1983. The following sections report the progress in uranium recovery research at PNL during the quarter.

This information is preliminary, and conclusions should be regarded as tentative. Further information will be contained in the topical reports published, or scheduled to be published throughout this research effort. The authors solicit comments and suggestions from readers of this progress report.

STABILIZATION, ENGINEERING, AND MONITORING
ALTERNATIVES ASSESSMENT FOR IMPROVING REGULATION
OF URANIUM RECOVERY OPERATIONS AND WASTE MANAGEMENT

Project Manager: M. G. Foley

FIN B-2370

OBJECTIVE

This research effort will address many of the technical issues related to providing and assessing methods for predicting, evaluating, and limiting the environmental effects of wastes from uranium milling operations. The principal objective of the project is to provide information essential in licensing actions to ensure that individuals and the public will be adequately protected during the active life of the mill and over an indefinite time period following shutdown. The scope of this investigation embraces seven tasks, each of which will be discussed separately in the report.

TASK 1. LONG-TERM STABILIZATION

Task Project Manager: W. H. Walters
Principal Investigator: W. H. Walters
Support Investigators: J. M. Doesburg
M. G. Foley
R. L. Skaggs
R. M. Ecker
P. A. Beedlow

FIN B-2370 (Task 1)

OBJECTIVE

Through this task we will provide the Nuclear Regulatory Commission with an engineering handbook on the protection of decommissioned uranium tailings impoundments from long-term erosion by wind and water. The handbook will also include a technical/economic evaluation of riprap design procedures, an evaluation of watershed models for estimating potential surficial erosion around the tailings pile, and criteria to estimate embankment slope stability.

ACCOMPLISHMENTS DURING THE PAST QUARTER

Subtask A. Technical Feasibility Study

1. Grand Junction, Colorado Case Study

The HEC-2 Colorado River Model for the Grand Junction site was finalized based on a comparison of the simulated water surface profile for the 500-yr flood with the 500-yr profile published by the Corps of Engineers. Estimates of peak discharges were made for six flood events based upon the Corps of Engineers' determination of the Colorado and Gunnison Rivers standard project floods (SPF) and a Bureau of Reclamation feasibility-level probable maximum flood (PMF) estimate at the Una Reservoir site upstream of Grand Junction.

The six flood event discharges were:

<u>Flood Event</u>	<u>Discharge (cfs)</u>	
1. Upper PMF	175,000	(2.5 x SPF)
2. Una Reservoir PMF	146,000	
3. Lower PMF	117,000	(1.67 x SPF)
4. 500-yr Flood	82,000	
5. SPF	70,000	
6. 100-yr Flood	63,000	

The analysis of the area flooded by PMF events indicates that the southern and eastern faces of the impoundment should be protected from the full force of the Colorado River floods while significantly less protection will be required on the remaining side slope surfaces. The upper PMF event does not

overtop the impoundment. Using hydraulic data derived from the river model, calculations using the Factor of Safety Method (Walters, 1983) were made to determine the rock sizes required for the Grand Junction site. The medium diameter rock size (D_{50}) calculated for the six flood events range from $D_{50} = 7.5$ in. (100-yr flood) to $D_{50} = 18$ in. (Upper PMF).

2. Slickrock, Colorado Case Study

A field reconnaissance of the slickrock site was conducted to determine the work necessary to obtain trans-flood-plain channel cross-sections of the Dolores River. Based on the site visit and an evaluation of project data requirements, the decision was made to obtain the cross-sections using a combination of aerial photogrammetry and field surveying. A detailed contour map of the flood plain was developed from aerial photography obtained during the low flow period of the river. River cross-sections below the water surface were obtained by profile leveling at the site.

A subcontract for aerial photogrammetric mapping of the site area flood plain was finalized with Aerial Photography and Global Engineering of Grand Junction, Colorado during July. Work commenced during August. Before the overflight, ten channel cross-sections were surveyed by PNL staff and targets set to mark their location for the aerial photography. The overflights were completed during the second week in August and the 2-ft contour topographic maps were received from the subcontractor during early October.

Subtask B. Riprap Design for Overland Erosion and Local Scour

The literature review has been completed for this subtask. No information was found on specific design criteria for using rock cover to prevent overland erosion. Designs will most likely be based on the degree of overland erosional processes active at the site. We expect that in many cases the local rock material readily available at the site, such as gravel and cobbles or talus material, will provide adequate protection.

Information found on local scour caused by high-velocity flows related primarily to the protection of bridge piers at stream crossings, river training embankments, and various other hydraulic structures. The literature indicated that most local scour protection is designed according to physical model studies of typical structures or site-specific cases. The results of this study will be used to provide guidance in selecting rock material to protect against overland erosion. Current practices used to estimate the extent of local scour will be summarized in the final handbook.

Subtask C. Riprap Protection for Local Drainage Channels

The literature pertaining to this subtask is currently being reviewed. To date, the review indicates that most of the information can be obtained from other design manuals and handbooks.

Subtask D. Vegetation Covers

During September the first draft of the NUREG document on vegetation covers was completed. Major topics in the report are: 1) impoundments as dynamic systems, 2) basic designs involving vegetation, 3) vegetation and the erosional process, 4) environmental constraints on vegetation, 5) the effectiveness of vegetation for controlling erosion on uranium tailings, 6) effects of rock material on vegetation and soil moisture, and 7) designing surface covers using vegetation.

The San Juan (New Mexico) test plots were sampled during August. The plots were originally set up for the Department of Energy by PNL for testing vegetation establishment in dry climates. Data were collected on both vegetation and soil moisture. Significant changes were observed in vegetation composition compared to the previous year. Weedy species were reduced, shrub species grew significantly, and grass cover increased. No irrigation water was applied during the second growing season. The decline in weedy species is probably a result of less water plus increased competition from perennial shrubs and grasses. Results from the second year indicate successful establishment of vegetation.

Subtask E. Economics of Riprap Design Procedures

This subtask uses the results from Subtask A (Technical Feasibility Study) and Subtask G (Rock Selection and Durability) to evaluate the cost of applying riprap to the Grand Junction and Slickrock sites. Rock size and volume requirements were analyzed for the six flood events computed in Subtask A considering several embankment side slopes. Haul distances were evaluated using the various sources of rock in the vicinity of the Grand Junction site. Preliminary results for the Grand Junction site indicate the optimum rock source is the Dakota Formation (sandstone) with a haul distance of about 2-1/2 miles. Riprap protection against river flooding for the impoundment would require the placement of about 53,500 cubic yards of rock assuming a side slope of 1V:6H. Work on the Slickrock site will start when the results of the Dolores River hydraulic model are available.

Subtask F. Watershed Model Evaluation

Work is scheduled to commence during December and be completed during FY-84.

Subtask G. Rock Selection and Durability

A field trip to investigate various rock sources near the Grand Junction and Slickrock sites was conducted during late June. Rock samples were collected and returned to PNL for laboratory testing of specific gravity and slake abrasion. The specific gravity of rock from each source was determined for design calculations in Subtask E (Economics of Riprap Design Procedures). The slake-abrasion testing phase of our study began during September. We

constructed a rock tumbling apparatus using specifications from the International Society for Rock Testing Mechanics Handbook. The basic design of the apparatus is a wire mesh tumbler that is partially submerged in water; rocks tumbled in this device are exposed in theory to an erosional environment more nearly approximating that of a stream. The rocks are tumbled, dried and weighed for five cycles and the percent weight loss between each cycle is calculated and plotted. Those rocks that show a small, consistent decrease in weight during each cycle appear to be durable, and their percent weight loss for a representative number of cycles can be used to over-size riprap composed of less-durable rock. Those rocks that suffer catastrophic weight loss during one of the cycles will be more likely to fail and are not likely to be suitable for use as an armor material.

Subtask H. Impoundment Slope Stability and Settlement

The literature review was started for this subtask during September.

REFERENCES

Walters, W. H. 1983. Survivability of Ancient Man-Made Earthen Mounds: Implications for Uranium Mill Tailings NUREG/CR-3061 (PNL-4541). Nuclear Regulatory Commission, Washington, D. C.

TASK 2: INTERIM STABILIZATION OF TAILINGS

Task Project Manager: J. N. Hartley
Principal Investigator: M. R. Elmore

FIN B-2370 (Task 2)

OBJECTIVE

The overall objective of this task is to assess the effectiveness, durability, and practicability of interim stabilization techniques and strategies for the suppression of dust from exposed tailings surfaces, under a full range of site and environmental conditions.

ACCOMPLISHMENTS DURING THE PAST QUARTER

A field test plan was developed to evaluate commercially available wind-screens for their potential in reducing fugitive dust, and to test additional chemical stabilizers that had been identified since the 1982 field test.

The field test was initiated at a uranium mill in Gas Hills, Wyoming, near the site of the 1982 field test to evaluate the durability of commercially available windscreen materials and new chemical stabilizers. The windscreens were erected and the chemical stabilizers were applied from September 6 through September 13, 1983.

Another field test of three windscreens is planned near Richland, Washington to allow frequent monitoring of the performance of the windscreen. Delays have been encountered in selection of a site for the test, but construction of the windscreen test began in October, 1983. The windscreen will be monitored for approximately one year.

A report of the 1982 field test of chemical stabilizers has been completed and sent to NRC for review and comment.

PROJECTED WORK FOR NEXT QUARTER

Activities for the next quarter will include installation of the wind screen field test at a PNL and monitoring of both the field tests. Work is also beginning on a report of laboratory testing of the chemical stabilizers.

REPORTS ISSUED DURING THE QUARTER

None.

TASK 3. TAILINGS DEWATERING TECHNIQUES

Task Project Manager: D. W. Mayer
Principal Investigator: D. W. Mayer
Support Investigators: T. J. McKeon
S. W. Tyler
T. W. Schrauf

FIN B-2370 (Task 3)

OBJECTIVE

In this task we determine the most effective approaches to dewatering uranium mill tailings that have been slurried into pits. Minimizing the release of contaminants to the environment by reducing the seepage into ground water and earlier placement of radon suppression covers are the primary objectives. Special attention is given to evaluating the classical vertical consolidation theory as a worst-case estimator of settlement during the dewatering of tailings. Improved analysis techniques will be implemented, and we will evaluate and test measurement techniques for obtaining the material properties (i.e., void ratio, degree of saturation and hydraulic conductivity) as functions of the stress-state parameters. We will use this analysis capability to assess various disposal strategies.

ACCOMPLISHMENTS DURING THE PAST QUARTER

Subtask A. Evaluation of Linear Consolidation Theory

The work on this subtask was completed in FY-82.

Subtask B. Measurement and Representation of Material Characteristics

The objective of this subtask is to obtain the necessary saturation, hydraulic conductivity and void ratio data that will allow us to simulate the fluid flow and consolidation in uranium mill tailings piles. We will also develop methods for interpreting the lab data.

Based on the findings from Subtask A, the appropriate lab apparatus for measuring the soil property data has been obtained. The equipment consists of the consolidation apparatus that is used for obtaining the data for saturated samples and the tri-axial test set that is used for measuring the soil characteristics of partially saturated samples. During the last quarter this equipment was installed. Modifications to the equipment were required to allow us to use it with hazardous materials (i.e., mercury and radioactive water). These modifications have been completed and initial testing with Ritzville silt-loam soil has been finished. The initial testing was designed to point out any additional modifications that might be required. Some minor changes were necessary and these have been made.

Methods for representing the soil properties as mathematical functions have been developed and a method for estimating hydraulic conductivities of partially saturated soils based on the saturation data has been implemented. Hydraulic conductivities for the partially saturated zone often must be estimated because this property is difficult to measure. Methods for measuring this property are documented in the report on the TRUST-II utility package report that was completed in August.

Subtask C. Computer Code Modification Testing and Documentation

The objective of this subtask is to change the existing consolidation model in the TRUST code to the two stress-state model. This change primarily involves making void ratio, saturation, and hydraulic conductivity a function of both the load at a point in the tailings pile and the local capillary pressure. This representation of the material properties will only be used in the partially saturated region. The classical consolidation theory, with the soil properties handled as functions of effective stress (i.e., the load minus the pore water pressure) will still be used in the saturated region. To meet this objective and to make the new technique available to others the new version of TRUST (which will be designated TRUST-II) along with a pre- and post-processor utility package will be tested and documented.

The major modifications to the TRUST-II code and the initial testing have been completed. We have simulated simple flow problems that have analytic solutions. These test problems demonstrate that the new consolidation model has not affected the accuracy of the TRUST code when simulating infiltration and drainage of a column of soil. The saturated consolidation portion of the code has also been successfully tested. As soon as partially saturated data become available from Subtask B, the testing of that portion of the TRUST-II model will be started.

The TRUST-II utility package consists of several programs that are useful for preparing input data for TRUST-II and for analyzing the results of the TRUST-II simulations. This package consists of a set of programs for analyzing soil property data, a grid generation program, and a program that is useful for analyzing the flow and transport of contaminants. We have successfully tested and documented this package. A report on the package was submitted in August.

Subtask D. Evaluation of the Interactions Between Consolidation and Fluid Flow

No work on this subtask was scheduled for this report period.

Subtask E. Tailings Dewatering Test Cases

No work on this subtask was scheduled for this report period.

PROJECTED WORK FOR NEXT QUARTER

During the first quarter of FY-84, the research to be performed will be measurement of the soil property data for slimes from the Grand Junction mill tailings pile. Documentation of the variably saturated flow and consolidation computer model TRUST-II will be continued.

The soil properties for the slimes will be used (during the second quarter of FY-84) in the comparison studies to be conducted under Subtask D. Because we expect the slimes to consolidate more than the other materials that will be measured (i.e., sand/slimes mix and overburden), we anticipate that the effects of coupling and decoupling the flow and consolidation will be significant. A letter report is scheduled for December, 1983. This report will include a discussion of the lab procedure used to obtain the soil properties. A summary of the measurements made to date will also be included along with any important findings regarding the measurement procedures. We plan to include the letter report as an attachment to the first quarter report for FY-84.

Additional testing of the TRUST-II model will be performed to insure that the new algorithm is working properly and does not adversely affect the accuracy of the model results. Once documented (scheduled for July, 1984) the model will be available for use by others to perform the simulation of flow and consolidation. It should be noted here that the utility package that was submitted in August, 1983 is compatible with the TRUST-II version of TRUST. The utility package was made compatible with TRUST-II to eliminate the need for redocumentation of the utility package once the TRUST-II model has been released.

REPORTS ISSUED DURING THE QUARTER

McKeon, T. J., S. W. Tyler, D. W. Mayer and A. E. Reisenauer. 1983. TRUST-II Utility Package: Partially Saturated Soil Characterization, Grid Generation and Advective Transport Analysis. NUREG/CR-3443, (PNL-4805), Pacific Northwest Laboratory, Richland, Washington.

TASK 4. TAILINGS NEUTRALIZATION AND OTHER ALTERNATIVES FOR IMMOBILIZING TOXIC MATERIALS IN TAILINGS

Task Project Manager: B. E. Opitz
Principal Investigators: B. E. Opitz
R. J. Serne
Support Investigators: M. E. Dodson
R. L. Erikson
M. J. Mason

FIN B-2370 (Task 4)

OBJECTIVE

In this task, we assess the effectiveness, benefits, and costs of treating acidic tailings and tailings solution to reduce the potential leaching of toxic elements, radionuclides and macro-ions from a tailings impoundment.

ACCOMPLISHMENTS DURING THE PAST QUARTER

Subtask A. Neutralization Methods Selection

This subtask was completed in FY-83, when we completed and submitted the literature review on amelioration techniques. However, throughout the remainder of the project we will make an effort to keep abreast of recent developments in applicable treatment techniques.

Subtask B. Laboratory Analysis

Laboratory experiments started this quarter to investigate a possible alternative to neutralizing the acidic tailings solution in an entire tailings impoundment. The studies, using flow-through permeability columns, involve add-mixing up to 5% (by weight) lime with onsite sediments from two Wyoming mills. These treated sediments, when compacted and used as a liner or in conjunction with a synthetic or natural liner form what is called a neutralizing barrier. The barrier, placed below the existing tailings pond bottom, neutralizes (treats) only the solution which escapes from the tailings impoundment.

Initial results from these experiments have shown dramatic decreases in permeability (values approaching 10^{-10} cm/s) as contact with the acidic (ph 2.0 or less) tailings solution continues. Untreated sediments (sediments with no lime) display permeabilities two to three orders of magnitude larger than those of treated sediments after periods of equal acid solution contact.

The advantages of this type of solution-treatment method are:

- acidic solution recycling is possible from the tailings pond to the mill circuit if desired
- only the solution which escapes from the designated tailings pond is

- the capital equipment expenditures, operating costs and maintenance of a system designed to treat discharged tailings solution before disposal into a tailings pond are eliminated.

The collected column effluent solutions are currently being analyzed. The results will indicate to what degree contaminant reduction or attenuation has initially occurred, and continued acid solution contact will provide the data for long-term evaluation of the neutralizing barrier.

Leaching experiments are being performed on solid tailings which were neutralized with lime to $\text{pH} \approx 7.0$. The treated tailings from two Wyoming mines are being contacted with laboratory-prepared ground water (a solution that is representative of the ground water found near the mill site) at a constant leach rate. The initial leaching results show that the only elements in significant concentration are those that are soluble in neutral solutions (i.e., Ca, Mg, Na, Cl, and SO_4). These test results will be compared with the data from earlier leaching studies on untreated acidic tailings. In those previous studies, the majority of hazardous constituents were leached (became mobile) within the early pore volumes of leachate contact. The leaching experiments will continue for several additional pore volumes of contact to evaluate the long-term effectiveness of neutralizing the solid fraction of the acidic tailings waste.

Subtask C. Field Tests

A field demonstration plan entitled, "Field Demonstration Plan for Verification of Uranium Mill Tailings Neutralization Technique," was submitted during the second quarter of FY-83. The plan outlines three alternatives for field testing the most promising and cost-effective current neutralization techniques.

PROJECTED WORK FOR NEXT QUARTER

We will continue our studies of long-term leaching through neutralized sludge and studies on contaminant migration through neutralizing barriers.

REPORTS ISSUED DURING THE QUARTER

Opitz, B. E., M. E. Dodson and R. J. Serne. 1983. Laboratory Evaluation of Limestone and Lime Neutralization of Acidic Uranium Mill Tailings Solution, (NUREG/CR-3449), (PNL-4809), Nuclear Regulatory Commission, Washington, D. C.

TASK 5. DISPOSAL TECHNIQUES ALLOWING CONTACT WITH GROUND WATER

Task Project Manager: R. W. Nelson
Assistant Task Manager: T. J. McKeon
Principal Investigators: A. E. Reisenauer
T. J. Bander

FIN B-2370 (Task 5)

OBJECTIVE

Within this task we are evaluating particular environmental concerns that may result from disposal of uranium mill tailings below the water table. Disposal below the water table may be of two major types. The first involves below-grade disposal in excavated pits where a significant part of the tailings is below the regional water table and is subject to long-term leaching by ground water. The second type involves deeper disposal of tailings in underground mine stopes below the water table.

ACCOMPLISHMENTS DURING THE PAST QUARTER

Significant progress has been made on a method to evaluate the environmental consequences of disposal of uranium mill tailings below the water table in deep mine stopes. The method uses analytical expressions for the velocity potential and examines the convective transport of tailings liquor and leachate through the aquifer into a water-supply well downgradient from the mine stope. The arrival distribution of contaminants (mass flux versus time) and the concentration of the contaminant in the water pumped from the well as a function of time are the final results of the analysis.

Our method is intended to be easy to use and is appropriate when a limited amount of data are available. Though many distributed-parameter models were already available for analyzing flow and transport in ground-water systems, we developed a specific idealized model to characterize the amounts, rates, travel times, and flow paths of the contaminants from a tailings filled stope transported by water. The models currently available are based on numerical techniques for solving partial differential equations over large heterogeneous domains. These distributed-parameter models require that a large amount of data be measured or estimated for each subregion of the domain and that the appropriate grid is developed to discretize the domain.

Because such detailed distributed data are seldom available, our method of analysis is based on an analytical model of flow through a single zone of different permeable material surrounded by an infinite homogeneous medium. The single zone is an idealized mine stope filled with uranium mill tailings with different permeabilities than the surrounding medium.

In analyzing the flow system, one of the most important considerations is the permeability contrast between the tailings in the mine stope and the surrounding medium. The contrast in permeability not only controls the relative

amount of ground water flowing into and through tailings, but also causes the pathlines of the ground water to be refracted when they cross through an area of different permeability.

The orientation of the mine stope with respect to the regional ground-water gradient is another very important parameter in defining the extent of the potential contamination problem. The regional groundwater gradient may intercept the stope at any angle from 0° to 90° with the longitudinal axis of the mine stope. The angle at which the regional gradient intersects the stope or tunnel is important because the size and duration of the down-gradient contaminant plume change significantly as the angle varies from 0° to 90° . For example, at 90° (when the regional gradient is perpendicular to the stope), the ground water moves directly across the stope so less water is contacted with tailings for leaching. This kind of direct seepage results in a downgradient leachate plume that is short but very wide (i.e., the plume is essentially as wide as the tailings-filled stope is long).

If the gradient is oriented at 45° to the tunnel length, the ground-water flow paths are diagonal through the tailings, which gives a longer flow path and a longer leachate plume. This results in a longer time period in which peak concentrations enter the pumped well downgradient from the tailings disposal tunnel. At the 45° orientation, the leachate plume is narrower, with a width about seven-tenths that of the tunnel length (i.e., approximately the projected tunnel length normal to the regional gradient).

The different lengths of the leachate plume and corresponding shorter or longer times for the plume to move past the downgradient well can significantly change the leachate concentration reaching the biosphere. The reduction in contaminant concentrations in the water pumped from the well depends both on the plume length and the flow pattern of the fluid into the well.

Contaminants at the front of the leachate plume arrive at the well earlier because they travel along the shorter more direct pathlines into the well. These contaminants are diluted as the contaminated water is mixed with clean water during pumping. The uncontaminated water preceding the leachate front, but traveling along the longer more indirect pathlines dilutes the contaminated water in the well that arrived along the shorter pathlines. Significant dilution occurs if the length of the leachate plume is less than the difference in length of the longest and shortest pathlines entering the well.

The chemical interactions with the ground-water flow occur in two important areas of the analysis. The first are those interactions that occur when ground water of given chemical composition leaches the tailings. The second area is the chemical interaction of the leachate with the aquifer material downgradient from the tailings. Only the first of these two chemical interactions, namely the leaching of the tailings, is currently incorporated in our analysis method. Specifically, we are using column-leaching data from laboratory experiments by scaling-up the values on a column-volume and residence-time basis.

Although the present model and analysis code has the capability to consider chemical interaction of leachate with aquifer material, such interactions are not considered at present. Before we can incorporate this factor in the model, we need data from coupled-transport and chemical modeling that will be done in FY-84.

PROJECTED WORK FOR NEXT QUARTER

Our major effort during the next quarter will be to complete and document the fluid-flow modeling and analysis method. Specifically, a NUREG document entitled, Evaluation Methods for the Consequences of Below-Water Table Mine Disposal of Uranium Mill Tailings, by T. J. McKeon and R. W. Nelson will be prepared to meet the Task 5 milestone due at the end of next quarter.

We will also begin testing the initial combined analysis of transport-geochemical interactions. The initial first-cut attempt at coupling was developed during the last year at PNL under limited sponsorship of another customer and will be initially tested for two uranium acid tailing geochemical systems. The testing will involve using uranium tailings experimental data coming from last year's work on this task and from NRC B-2292. Experimental column data from these studies are available to provide testing of the initial geochemical transport model. If adequate agreement is found between the calculated and experimental chemical breakthrough results, then the coupled transport-geochemical evaluations will be incorporated into the detailed tailings analyses of disposal below water table.

TASK 6: EFFLUENT AND ENVIRONMENTAL MONITORING METHODS
AND EQUIPMENT AND INSTRUMENT TESTING

Task Manager: N. A. Wogman
Principal Investigators: P. O. Jackson
E. A. Lepele
K. B. Olsen
V. W. Thomas
W. C. Weimer
J. A. Young

FIN B-2370 (Task 6)

OBJECTIVE

In this task we assess measuring devices, techniques, and procedures for verifying if site and structure decontamination is acceptable. We develop needed monitoring methods and equipment, including methods to assess the release of radioactive and toxic materials from various facility components. From these assessments, we can provide guidance on monitoring requirements and strategies to evaluate compliance with uranium mill and tailings standards (e.g., PL-95-604, 40 CFR 192, 40 CFR 190). The work in this task is distributed among several subtasks identified below.

ACCOMPLISHMENTS DURING PAST QUARTER

Subtask A. Field Comparison of Radon Progeny Measurement Techniques and

Subtask C. Critical Evaluation of Long-Term Radon-Daughter Measurements and Needed Improvements

Objective

These two subtasks have been completely integrated. This includes the field comparison of short-term and long-term radon and radon-daughter measurement techniques in two test houses in Edgemont, South Dakota and preparation and issuance of the combined status report. Below we have listed the objectives of subtasks separately. In future progress reports we will refer to the integrated subtasks as Subtask A.

Subtask A -- In this subtask we ascertain whether a satisfactory short-term measurement technique is available for the determination of annual-average radon-daughter concentrations in buildings.

Subtask C -- We are to determine which, if any, of the available long-term radon and radon-daughter measuring devices is the most accurate and cost-effective.

Accomplishments During Past Quarter

During September, an occupied house and a vacant house were instrumented to measure radon-daughter concentrations and other parameters that could affect the radon-daughter concentrations. A weather station, set up about 30 feet from the vacant house, is measuring temperature, pressure, and windspeed and

direction. Average values are reported for 15 minute intervals. Radon-daughter concentrations are measured every 30 minutes in both the vacant and the occupied houses using alphaNUCLEAR¹ radon-daughter analyzers. Average radon-daughter concentrations are being measured weekly at the same locations using Radon Progeny Integrating Sampling Units (RPISU). Duplicate Terradex (both type B and type F) Track Etch[•] detectors have been placed at several locations in each house to determine long-term average radon and radon-daughter concentrations.

Eberline² radon analyzers are being used to measure average radon concentrations over 15-minute intervals at the locations of the alphaNUCLEAR analyzers. Condensation-nuclei (CN) counters were also installed at the same locations to measure average CN concentrations over 15-minute intervals. However, the CN counter in the vacant house malfunctioned and had to be removed for repair. The average temperature in the occupied house is being measured over 15-minute intervals. The time periods that a ceiling fan, a fan over the kitchen stove, and a furnace fan are in operation are also recorded. A humidity measuring device is also being installed in the occupied house.

A helium-leak detector is being used to measure the rate of exchange between inside and outside air in both the occupied and vacant houses. Whenever the helium concentration in either house falls below a given value, helium is automatically added to that house from a helium cylinder. Sniffer probes are then used to sample the air for measurement of the rate of decrease in the helium concentrations in the houses. Every thirty minutes the average helium concentration over a 5-minute interval is measured in the occupied house and the vacant house, outside, and from a standard source. So far these measurements indicate that the rates of decrease in the helium concentrations in the two houses are very regular although different from each other. The helium is introduced into the air-circulation system of the furnace of the occupied house and the furnace fan is automatically turned on for 15-minutes to distribute the helium. Simultaneous helium measurements in the basement and the first floor of the occupied house indicated that the helium becomes distributed very rapidly throughout the house. The helium in the vacant house is introduced through a manifold into four rooms of the house and is distributed through the house by four floor fans that turn on automatically whenever helium is added.

The data from these measurements are transmitted via telephone modem from a data logger, which collects the data in Edgemont, to a hard-disk storage unit in the computer room in Richland, Washington.

Projected Work for Next Quarter

Some instrument problems will be corrected and data collection will be continued. The status report, "Critical Evaluation of Short- and Long-term Radon-Daughter Measurement Techniques and Recommended Procedures," will be written even though the data collection period has been extremely short. We were delayed in setting up the instrumentation because of manufacturing and software-writing delays for this state-of-the-art instrumentation.

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1. alphaNUCLEAR, Mississauga, Ontario, Canada.
 2. Eberline Instrument Corporation, Santa Fe, New Mexico.
 - Track Etch is a registered trademark of the Terradex Corporation, Walnut Creek, California.

Reports Issued During the Quarter

None.

Subtask B. Yellowcake Emission From Ventilation Exhausts

Objective

In this subtask we are to evaluate current methods for monitoring yellowcake and to recommend a new, revised, or improved method for monitoring yellowcake emissions from ventilation exhausts at uranium mill sites.

Accomplishments During Past Quarter

As part of the ongoing laboratory evaluation of selected methods for analyzing yellowcake, the use of x-ray fluorescence analysis (XRF) using isotopic activation sources has been investigated. Cadmium-109 and ^{57}Co appear to be the most feasible choices of isotopic sources. We prefer ^{57}Co because it has the most energetic gamma-ray (122 keV), and thus less absorption of the K x-ray (98 keV) of uranium would occur. However, the short half-life (0.7 years) and greater radiation-protection requirements for personnel must be considered. On the other hand, using ^{109}Cd would mean that the L x-rays (14 and 17 keV) would be used in the analyses. Their range would be much shorter than the K x-ray because absorption would occur in either the collection substrate or the sample. Therefore, absorption due to either the collection substrate or due to particle loading would need to be quantified. An advantage of the ^{109}Cd source is the longer half-life (1.2 years).

A 20-millicurie ^{109}Cd source configured as a ring has been evaluated for use with an 80-millimeter Si(Li) detector (resolution of 200 eV at 6.4 keV) coupled to a Canberra Series 80 multichannel analyzer. The absorption of the 14 and 17 keV L x-rays by Whatman-41 filter material appears to be negligible. Uranium standards were prepared by absorbing uranium solutions containing from 1 milligram to 35 milligrams into cellulose material which were then dried and pressed into wafers. These standards were used to prepare a calibration curve of the instrument response corrected for cellulose material present plotted against particle loading. An equation was then derived to describe the calibration curve.

Filter samples with masses of 0.4 to 20 milligrams of yellowcake were prepared by vacuum deposition of an aerosol. They were then analyzed and calculated using the calibration curve described above and compared to the expected particle loading. If we ignore possible sample loss in the pre-analysis preparation procedures (probably less than 5%), the ratio of experimental to expected values for particle loading of 0.4 to 20 milligrams is 94 with a standard deviation of 15.

Projected Work for Next Quarter

A ^{57}Co source will be evaluated in a manner similar to that used for the ^{109}Cd isotopic source evaluation. The use of a NaI(Tl) detector will also be evaluated because it would be preferable to eliminate the use of liquid nitrogen required for the Si(Li) detector. A status report, "Laboratory Evaluation of Instrumental Methods for the Measurement of Yellowcake Emission," will be issued.

Accomplishments During Past Quarter

All field testing was completed during the quarter. This included one trip to Edgemont, South Dakota during which 12 boreholes were drilled and logged with a downhole NaI(Tl) detector and a downhole intrinsic-germanium (IG) detector. Four residence properties were investigated. These included three residences that were contaminated with various levels of tailings and one uncontaminated residence. In addition to the well-logging measurements, soil samples were taken from the top 12-in. layer of soil. These samples were canned on site and shipped to PNL for further analysis. The goals of this trip were 1) to determine if the downhole detector is capable of estimating the concentration of ^{226}Ra at the surface (0-12 inches), 2) to determine if major shifts in equilibrium occur when a hole sits idle for a few hours to a day (this is very important when a NaI(Tl) detector is used to measure radon daughters) and 3) to determine if a downhole IG detector can give accurate estimates of ^{226}Ra concentration at the 5-15 pCi/g range in a reasonable amount of time.

The final field trip was made to the Grand Junction Technical Measurements Center. The purpose of this trip was to cross calibrate our calibration facility with the Grand Junction facility. The downhole IG detector was calibrated at this facility. This included the determination of water correction factors, the variations caused by borehole diameter, and calibration using the KUT (Potassium-Uranium-Thorium) model.

Projected Work for Next Quarter

We will complete the analysis of the data from the last two field trips and complete the final report on recommended well-logging procedures for use on remedial action programs.

Reports Issued During the Quarter

None.

Subtask F. Evaluate and Recommend Sampling Strategies for Temporal and Spatial Evaluation of Contamination

Objective

In this subtask, we are to develop guidelines to help detect and evaluate the windborne-radioactive contamination that has been spread from uranium tailings piles and which may extend up to several kilometers. Our guidelines will define the number, distribution, and timing of samples necessary to detect the spread of contamination with reasonable certainty, while keeping the cost and size of the detection effort at a minimum.

Accomplishments During Past Quarter

A topical Report, "Recommended Sampling Strategies for Spatial Evaluation of Windblown Contamination Around Uranium Tailings Piles," NUREG/CR-3479 (PNL-4830) was sent to NRC for publication on September 7, 1983. The following paragraphs summarize the contents of that report.

Pacific Northwest Laboratory has reviewed sampling and radiological survey strategies in the literature that are applicable to the detection and

Reports Issued During the Quarter

None.

Subtask D. Critical Evaluation of Measurement Techniques for Uranium, ^{226}Ra , ^{230}Th , and ^{210}Pb in Effluents and Environmental Materials and Recommended Improvements

Objective

In this subtask we compare the sensitivity of existing analytical procedures for quantifying U, ^{226}Ra , ^{230}Th , and ^{210}Pb in effluents and environmental materials. The individual sensitivities will be compared with regulatory standards. Where improvements are required, existing techniques will be extended, if possible, or new techniques will be developed to produce methods which are sensitive enough to address the regulatory standards. The final report for this sub-task will be a set of analysis methods to be used to measure the radioisotopes of interest in both effluents and environmental materials.

Accomplishments During Past Quarter

The shielding for two large surface-area (1900 mm^2), planar intrinsic-germanium detector systems has been modified by using readily-available plastic phosphors, which are operated in an anti-coincidence mode. The testing of this configuration to evaluate whether the detection limits for the isotopes of interest have been reduced is nearly complete.

Projected Work for Next Quarter

Testing of the anti-coincidence-shielded intrinsic-germanium detectors will be completed. A status report, "Measurement Techniques for Uranium, ^{226}Ra , ^{230}Th , and ^{210}Pb in Effluents and Environmental Materials Associated with Uranium Recovery," will be issued. This report will present 1) a comparison of existing analytical procedures, 2) a discussion of possible improvements in sample collection and/or analytical sensitivity, and 3) a recommendation for field and laboratory measurement procedures.

Reports Issued During the Quarter

None.

Subtask E. Review Well-Logging Techniques

Objective

In this subtask we are to 1) evaluate and compare well-logging techniques with core-sample analytical results for the measurement of uranium and its progeny in uranium tailings, 2) determine the effects of interferences (high natural concentrations of uranium decay-chain products and variations of ^{40}K concentrations) on the response of the well-logging instruments, and 3) recommend an acceptable procedure which can be applied to present and future uranium-mill tailings remedial-action programs.

delineation of windblown uranium mill tailings in the vicinity of uranium mill tailings piles. To support the requirements of the Uranium Mill Tailings Act of 1978, an optimum sampling strategy is proposed based on an analysis of the published strategies reviewed and a statistical analysis of an existing data base.

A portion of the data on ^{226}Ra concentration in soil collected in the Cottonwood district of Edgemont, South Dakota, was chosen as the data base. Data suspected of originating from sources other than windblown contamination were not used. These data were collected as part of the Edgemont Remedial Action Program.

Linear regression analysis of delta measurements made in Edgemont near tailings piles with a collimated, lead-shielded gamma scintillometer (micro-R-meter) and ^{226}Ra concentrations measured in soil-core samples, gave low coefficients of determination (coefficient of correlation squared). These analyses indicated that collimated micro-R-meters may ascertain the presence or absence of contamination above average background levels in the general vicinity of uranium mill tailings storage piles. However, the results also show that it would be more appropriate to use soil sampling or some other technique to make these same determinations for samples taken close to tailings piles.

Kriging, a geostatistical technique for estimating average concentrations at points or blocks over space, was applied to the Cottonwood data base. The spatial distribution and the total inventory of ^{226}Ra , of ^{226}Ra above background, and of ^{226}Ra above 5 pCi/g in the Cottonwood study area were estimated. We also determined that for situations like that at Cottonwood, the relative error in concentration estimates for blocks made with Kriging increases very slowly with larger grid spacing. Hence, using a large grid and few samples does not cause much loss in efficiency. However, a two-stage soil sampling strategy using Kriging would be required to be reasonably assured of differentiating residual radioactive material from natural material in 100-m² areas containing average ^{226}Ra concentrations greater than 5 pCi/g above background (the final EPA standard). A few samples on a wide-grid spacing would identify areas where more intensive sampling should be performed. A second sampling on a smaller grid in areas selected from the first Kriging would accurately identify the 100-m² areas that exceed the 5 pCi/g standard. An illustrative example is shown in the report that identifies areas in the Cottonwood tract which exceed the 5 pCi/g standard due to windblown tailings. Contour maps of ^{226}Ra in the study area, generated by the Kriging technique, are included. In the example, this two-stage sampling strategy would result in a 35% savings in sampling effort over that required to accomplish the same end with a single sampling.

The detection of both hot spots and windblown tailings requires that a regular grid of sampling points be used and that the grid spacing be approximately equal to the longest dimension of the hot spot. This would find (with greater than 75% probability of detection) a circular or elliptical hot spot near or on the surface.

General procedures are described for differentiating between residual radioactive material, uranium byproduct material, and native deposits of material naturally enhanced in uranium decay-chain products.

Projected Work for Next Quarter

The balance of work to be completed under this subtask will be deferred until additional funding is made available. This work includes application of the recommended sampling strategies presented in NUREG/CR-3479, to surveys of windblown tailings at one or more inactive tailings sites scheduled for remedial action. This will hopefully be conducted concurrently with surveys being performed by the remedial action contractor for the Uranium Mill Tailings Remedial Action Program and be conducted in coordination with field-verification studies needed under Subtasks D and G, which have also been deferred due to lack of funding. In addition we have recommended further evaluation of data from multiple surveys of selected uranium mill tailing sites published by others to select one or possibly two sites to revisit. Field measurements will be made to supplement existing data and to allow comparisons between sequential surveys. This will allow us to make temporal evaluations of sampling strategies over time.

Reports Issued During the Quarter

A topical Report, "Recommended Sampling Strategies for Spatial Evaluation of Windblown Contamination Around Uranium Tailings Piles," NUREG/CR-3479 (PNL-4830), by V. W. Thomas and R. R. Kinnison was issued.

Subtask G. Sampling Techniques for Detecting Contamination of Surface and Ground Water by Tailings Leachate

Objective

In this subtask we are to evaluate the existing standard techniques for measuring levels of contaminants in natural waters to determine their applicability at uranium recovery sites. Known dissolved contaminants that are potential hazards to water quality will be considered in this study. These include some of the radioactive uranium daughter products (in particular thorium and radium) and stable elements Se, As, Sb, Zn, Ni, Cr, and Cu. An additional objective is to propose a spatially-oriented monitoring protocol for ground water that will be generally useful for uranium recovery sites.

Accomplishments During Past Quarter

A subset of the data in the Hanford ground water monitoring program has been selected to test a number of sampling strategies. Variables being evaluated are well placement, number of wells, and times of sampling. During this past quarter we have examined the data in this subset and have verified or deleted the questionable data points in order to produce a data base suitable for statistical analysis.

Projected Work for Next Quarter

A geostatistical technique (Kriging) will be used to handle the selected data set. This approach will help define the number of sampling locations required to estimate contaminant inventory and concentration distribution. A status report, "Evaluation of Sampling Techniques for Detecting Contamination of Surface and Ground Waters by Tailings Leachate," will present 1) an assessment of available analytical methodologies for measuring selected stable elements and radioactive uranium daughter products in natural waters, 2) a procedure for monitoring surface and ground waters near uranium recovery sites, and 3) the statistical evaluation of the development of this procedure.

Reports Issued During the Quarter

None.

Subtask I. Radon Flux Comparisons with ^{226}Ra Concentrations in Surface and Subsurface Soils

Objective

We will examine the degree of correlation that exists between radon fluxes and ^{226}Ra concentrations in surface and subsurface soil to determine whether average radon fluxes can be predicted from measurements of ^{226}Ra concentrations in soil and whether detection and delineation of subsurface deposits of ^{226}Ra can be enhanced by the use of radon-flux measurements at the soil surface.

Accomplishments During Past Quarter

A total of 100 flux measurements were made in September at locations on three properties at Edgemont that were as close as possible to the locations at which fluxes were measured in June of 1983. Fifty-four of these measurements were made at the grid points of a rectangular grid on a property that was known to contain residual radioactivity to determine the variation in the flux with time and to determine how well the average flux from the property in September could be determined from individual flux measurements in September and measurements that were made in June using the following formula.

$$\text{Average flux (September)} = \text{individual flux (September)} \frac{\text{average flux (June)}}{\text{individual flux (June)}}$$

We found that the coefficient of variation of the average fluxes calculated from single measurements was about 50%. Preliminary calculations indicate the coefficient of variation of the average flux calculated from pairs of measurements was about 43% and for three measurements was about 25%. These results suggest that if the average flux from an area was determined at one time from measurements at the grid points of a 10-foot rectangular grid, a fairly good estimate of the average flux could be made at a later date from a limited number of measurements at a few of these grid points.

At several of the locations, three charcoal canisters were set out in a line with about 6 inches between the centers of the 3-inch diameter canisters. We found that the coefficient of variation between the triplicate measurements averaged about 15%.

Flux measurements were also made around the circumference of two houses that had elevated indoor-radon-daughter concentrations, but where no other evidence of residual radioactivity was found to determine whether there was any residual radioactivity present that could be detected by flux measurements. Flux measurements in June showed elevated fluxes at a few locations. However, it appears that the measurements in September failed to confirm the presence of elevated fluxes at these locations. This indicates that the elevated fluxes resulted from natural variations in the measurements rather than residual radioactivity.

Projected Work for Next Quarter

Further field measurements of flux will be made to augment the data already collected. Conversations have been initiated with the Colorado Department of Health, the Department of Energy, and Rancher's Exploration Company of Albuquerque, New Mexico to seek authorization to make radon-flux measurements, gamma-ray dose measurements, and collect surface and source materials for measurements of ^{226}Ra concentrations at the Durita tailing piles near Naturita, Colorado. The Durita piles are unique because they have a uniform source material and they are capped with a relatively uniform layer of clay and topsoil. Therefore, it would be expected that variations in flux measurements and in particular gamma-ray dose-rate measurements would result in the most part from variation in thickness of cover material and/or imperfections in that material. Integration of the results of these measurements on the Dorita piles with results of measurements made at other locations would allow us to better define the relationships between these three parameters.

The report, "Comparison of Radon Fluxes with Gamm-Ray Exposure Rates and Soil ^{226}Ra Concentrations" will be written.

Reports Issued During Quarter

None.

TASK 7. TECHNICAL PROGRAM MANAGEMENT

Project Manager: M. G. Foley
Principal Investigators: M. G. Foley
G. W. Gee

FIN B-2370 (Task 7)

OBJECTIVE

This task provides the program management function of all the uranium recovery waste management studies contracted to PNL from the Waste Management Branch, NRC-RES. The principal functions of Program Management are to coordinate the efforts of scientists and engineers assigned to tasks, prepare and issue quarterly technical and administrative reports, maintain an awareness of uranium waste research by others, schedule and arrange local and external research reviews, and carry out related management functions.

ACCOMPLISHMENTS DURING THE PAST QUARTER

The program manager is the principal point of contact between the PNL technical team and NRC-RES project and task managers, and must ensure that PNL work addresses the research needs of the NRC; that NRC is kept informed of PNL progress as well as final products; and that all deliverables provided to NRC have been properly reviewed. Specific activities over the past quarter to accomplish this task are listed below.

- Submitted a 189 for FY-84 for B-2370, and prepared and submitted a revised version based on NRC comments and changes in program direction and scope.
- Submitted 189s for projects B-2292 (Leachate Assessment) and B-2379 (Methods for Minimizing Ground-Water Contamination In In Situ Leach Uranium Mining).
- Revised FY-83 work plans and scope to expend a supplemental \$115K for FY-83 and to complete FY-83-funded work by December, 1983.
- Prepared and submitted an analysis of the impact of program termination after FY-84 and FY-84 budget reduction and redirection on NRC's uranium licensing mission.
- Prepared and submitted an analysis of the impact of the newly-promulgated EPA regulations (EPA CFR 192) for active sites on NRC's need for additional research.
- Arranged and participated in an NRC review of the uranium recovery

- Reviewed the drafts and final documents of the reports produced by the uranium recovery program (listed elsewhere in this report).
- Prepared and submitted 3 monthly administrative reports.

PROJECTED WORK FOR NEXT QUARTER

In addition to managing the technical and budgetary schedules, and submitting periodic administrative and technical progress reports, the program manager will ensure that:

- The status of uranium recovery waste technology will be addressed, and short-term and long-term research needs determined so that the PNL program properly meets the needs of NRC-RES or addresses the impact of changing regulatory requirements on research needs if beyond the scope of the present program.
- Continuing reviews of PNL work by internal and external peer reviewers and by NRC will be arranged and conducted.

REPORTS ISSUED DURING THE QUARTER

Foley, M. G. et al. 1983. Uranium Recovery Research Sponsored by the Nuclear Regulatory Commission at Pacific Northwest Laboratory: Annual Progress Report, May 1982 to May 1983. (PNL-4608-3), Pacific Northwest Laboratory, Richland, Washington.

ATTENUATION OF RADON EMISSION
FROM URANIUM MILL TAILINGS

Project Manager: N. A. Wogman
Principal Investigator: D. R. Kalkwarf
Support Investigators: V. C. Rogers and K. K. Nielson
(Rogers and Associates
Engineering Corporation, RAE)

FIN B-2269

OBJECTIVE

In this project we will define uniform methods for determining the thickness of soil cover material needed to meet radon flux limits (as specified in connection with the final GEIS on uranium milling), and design methods for measuring the effectiveness of the soil cover after it is emplaced. These methods will be used to develop an NRC regulatory guide.

ACCOMPLISHMENTS DURING THE PAST QUARTER

TASK 5. Assess the Influence of Defects on Radon Diffusion in Cover Soils

Objective

In this task we are to 1) determine the size, shape, and frequency of defects in a soil cover which can significantly alter the radon-attenuating ability of the cover, 2) test the validity of radon-diffusion equations to predict the flux of radon through defective soil covers, and 3) identify soils to be avoided as cover material because of their proclivity to form cracks.

Accomplishments During the Past Quarter

A camera-ready copy of the report, Influence of Cover Defects on the Attenuation of Radon with Earthen Covers, NUREG/CR-3395, describing the results of this task, was sent to NRC this quarter.

Task 8. Prepare a Handbook for Determining Radon Attenuation Cover Soils (RAE)

Objective

We are to prepare a handbook to guide engineers in the covering of uranium mill tailings piles with soils in order to reduce radon emission to prescribed levels.

Accomplishments During the Past Quarter

An updated version of A Handbook for the Determination of Radon Attenuation Through Cover Soils, NUREG-CR-2340, was prepared and retitled, Radon Attenuation Handbook for Uranium Mill Tailings Cover Design, NUREG/CR-3533. A draft of this document is currently undergoing peer review.

Task 10. Validate Calculated Radon Attenuation Values for Soils Covering Large Areas of Tailings

Objective

We are to validate radon attenuation values, calculated by methods described in the revised engineering handbook, for large areas of tailings.

Accomplishments During the Past Quarter

Two types of earthen covers over uranium mill tailings at the test site in Grand Junction, Colorado, were sampled to obtain additional data with which to test the validity of the 'handbook' methods. Radon flux was measured at the surface of the covers as well as porosity, moisture content, and radon diffusion coefficient of the covers. The radon emanation coefficients, diffusion coefficients, moisture contents, and porosities of the tailings were also measured as well as their radium content. These values will be compared with those measured when the covers were applied two years ago, and all data will be intercompared by means of the 'handbook' methods.

Task 11. Describe Advective Radon Transport Through Cover Soils RAE

Objective

We are to evaluate the advective transport of radon with water vapor in soils and to assess the advection of radon in dry air resulting from changes in temperature and atmospheric pressure.

Accomplishments During the Past Quarter

A camera-ready copy of the report, The Effects of Advection on Radon Transport Through Earthen Materials, NUREG/CR-3409, describing the results of this task, was sent to NRC this quarter.

Task 12. Prepare a Regulatory Guide for Determining Radon Attenuation by Cover Soils (RAE)

Objective

We are to prepare a document in the format of an NRC Regulatory Guide that specifies acceptable methods for covering uranium-mill tailings with soil to reduce radon flux to within prescribed limits.

Accomplishments During the Past Quarter

A draft of this document has been prepared and is undergoing peer review.

PROJECTED WORK FOR NEXT QUARTER

This project is scheduled for completion in CY-83. During the remaining time we will deliver the following products to NRC.

- a camera-ready copy of Radon Attenuation Handbook for Uranium Mill Tailings Cover Design
- a camera-ready copy of a topical report describing tests of the validity of handbook methods using data collected at the Grand Junction site
- a camera-ready copy of a draft regulatory guide for determining radon attenuation by cover soils.

REPORTS ISSUED THIS QUARTER

Kalkwarf, D. R. and D. W. Mayer. 1983. Influence of Cover Defects on the Attenuation of Radon with Earthen Covers. NUREG/CR-3395 (PNL-4776), Nuclear Regulatory Commission, Washington, D. C.

Rogers, V. C., K. K. Nielson, G. B. Merrill, and D. R. Kalkwarf (project manager). 1983. The Effects of Advection on Radon Transport Through Earthen Materials. NUREG/CR-3409 (PNL-4789), Nuclear Regulatory Commission, Washington, D. C.

ASSESSMENT OF LEACHATE MOVEMENT FROM URANIUM MILL TAILINGS

Project Manager: S. R. Peterson
Principal Investigators: R. J. Serne
W. J. Martin
S. R. Peterson
M. E. Dodson
Support Investigators: M. J. Mason
G. W. Gee
B. E. Optiz

FIN B-2292

OBJECTIVE

Within this program we will develop experimental and computer modeling tools to assess the long-term environmental impact of leachate movement from uranium mill tailings.

ACCOMPLISHMENTS DURING THE PAST QUARTER

Task 1. Project Management

On July 22 a review of this project was conducted at PNL as part of a comprehensive review of the NRC uranium mill tailings and low level waste programs. The review involved PNL staff associated with the above programs and George Birchard from the NRC. The questions and discussion indicated no problems with the direction or emphasis of this project.

S. R. Peterson presented a paper at the annual meeting of the American Society of Agronomy August 17 in Washington, D. C. The presentation was entitled, "Interactions of Acid Solutions With Neutral Sediments in a Flow-Through System: Predictive Geochemical Modeling of Precipitation/Dissolution Reactions." In addition, an abstract of the presentation was published. A. R. Felmy and R. J. Serne were coauthors on both the presentation and published abstract.

S. R. Peterson was also invited to participate in and present a paper at the annual NRC geochemistry review in Reston, Virginia. The presentation was entitled, "Geochemical Modeling: A Case Study". A draft paper was also prepared to be included in a special NRC publication. Both the presentation and draft paper dealt with how laboratory experiments, geochemical modeling, and field studies have been used in our project to complement one another and, thus, reinforce the conclusions at which we have arrived.

The NUREG topical report, Predictive Geochemical Modeling of Interactions Between Uranium Mill Tailings Solutions and Sediments in a Flow-Through System, was delivered to the NRC and published this quarter.

A new 189 for Leachate Assessment was written this quarter which was to have encompassed work to be completed during fiscal year 1984. After drafting

this 189, we learned that our program would no longer be funded under the Uranium Recovery Program. Therefore, we wrote a proposal that was addressed to Low-Level Waste, because we feel the tools we are developing are of a generic nature. We have received assurances that our program will be funded under Low-Level Waste during the coming fiscal year.

Task 2. Laboratory Analysis and Experiments

The eight permeability-column experiments were finished. Two of the columns were packed with shaft wall material from a mine in New Mexico. We also packed duplicate columns with the overburden from two Wyoming mines, and coarse shaft wall material from another mine. The columns were leached with ground water to establish a chloride-background baseline. Once the chloride baseline was established, the columns were injected with chloride spikes, and effluent chloride concentrations were monitored to provide data to compute the dispersion coefficients for these coarse materials.

The column experiments designed to measure the 'scaling up' effects were finished. These columns were leached with acidic tailings solution. The column effluent solutions are currently being analyzed and the analyses should be complete within the month.

Task 3. Geochemical Modeling

A solid-phase assemblage was used to represent a soil column and to predict the aqueous effluent compositions from columns of subsoil materials percolated with uranium mill tailings solutions. Previous geochemical modeling efforts (Nordstrom et al. 1979; Gang and Langmuir 1974; Jenne et al. 1980; Peterson and Krupka 1981; Peterson et al. 1982; and Deutsch et al. 1982) were confined to examining saturation indices in the quest for solid phases that could be in equilibrium with their dissolved constituents. Little effort has been expended to use these solid phases as a model of a heterogeneous material. Such a mineral assemblage can be reacted with a specified solution in a flow-through system and used to predict the resultant effluent concentrations. The solid-phase assemblage was constructed not only from calculations of ion speciation/solubility, but also from our understanding of the chemical processes occurring in the system.

In the experiments we modeled, columns of various configurations were packed with subsoils (either a silty clay loam or a sandy loam) and leached with one of two uranium mill tailings solutions. The two solutions were taken from the same site, but differed in composition. The uranium mill tailings solution contacted the aforementioned sediments for periods varying from 3 weeks to approximately 3 years, depending upon the specific experiment. Transit times for a single pore volume of solution varied from 18 hrs to roughly 45 days in the vacuum extractor and permeability columns, respectively. We compared measured effluent concentrations to predicted effluent concentrations, not only to judge the adequacy of the postulated mineral-phase assemblage but also to better understand important chemical mechanisms.

We presented our initial predictive modeling effort in this report to illustrate the methodology employed in predictive modeling and for demonstrating the applicability of this type of modeling to the movement of leachate from uranium mill tailings impoundments. We will continue to try to refine the conceptual model to increase the accuracy of the models. These efforts will be documented in reports.

Using precipitation/dissolution reactions considered in the conceptual model we were able to predict the column-effluent concentrations of several of the macro constituents of the tailings solutions (SO_4 , Ca, Al, Mn, and Fe). Sulfate concentrations in the column effluents were generally one to two orders of magnitude above the secondary drinking water standards established by the U.S. Environmental Protection Agency. The conceptual model was able to predict these elevated concentrations.

The conceptual model was unsatisfactory when used to predict the concentrations of selected trace metals. Generally, trace metals were undersaturated relative to any solid phases that could control their concentrations. However, data developed through laboratory and field studies lead us to believe that we can empirically quantify the migration of trace metals. Other mechanisms besides precipitation/dissolution (e.g., adsorption, ion exchange) appear to be controlling the concentration of many of the trace elements. Additional laboratory data must be developed to adequately predict the concentrations of these trace elements. Precipitation/dissolution reactions based on thermodynamic constants account for the effluent concentrations of some elements, but additional mechanisms, for which experimental data must be developed, are necessary to explain the effluent concentrations of others.

The concentrations of many trace elements appear to be controlled by adsorption and/or coprecipitation with ferric oxyhydroxide surfaces. Several adsorption models of the hydrous-oxide water interface have been formulated (Davis and Leckie 1978; Hohl and Stumm 1976) and are considerably successful in modeling the adsorption of trace metals onto hydrous oxides. In addition, intrinsic-stability constants for the reaction of several trace metals with iron oxyhydroxides have been published in the literature (Davis and Leckie 1978; Leckie et al. 1980; Balistireiri and Murray 1982). Thus, it appears that the conceptual chemical model presented here can be expanded to predict the adsorption of several trace metals onto the surface of iron oxyhydroxides.

We began geochemical modeling using the samples collected at a mine near Riverton, Wyoming. Initially, we will calculate ion-speciation solubility. Future work will involve constructing a chemical model to explain the concentrations of various contaminants as the tailings solution migrates from the disposal pond.

Task 4. Field Study

A trip was made to a mine in Gas Hills, Wyoming, to obtain data/data sets that could be used in a geochemical model validation effort. In particular we were interested in the data related to seepage from tailings pond #1. This pond has a rather detailed history of seepage and well-documented

records of ground-water quality. The mine personnel were very helpful and open about providing reference materials, raw data, and reports that were of interest to us. During this visit we met with the mine's Resident Manager and 3 TVA employees and discussed the NRC field study work. The TVA people seemed satisfied that our work was in their best interest and the resident manager indicated that we could have free access to the available data.

The pond is now inactive and almost completely drained. However, after reviewing the data, we believe enough information is available to estimate past seepage rates. The contaminant plume from tailings pond #1 is well defined and the well logging and water quality measurements have been taken periodically for the past two years. These measurements are being continued. Based on the cooperation of the mine personnel, it seems appropriate to use this site for a field study. We can supplement the available data with additional data that we will collect onsite.

PROJECTED WORK FOR NEXT QUARTER

Efforts in FY-84 will concentrate on field site surveys to collect necessary and sufficient geochemical and hydrologic data on ground water, tailings, tailings solutions, liners, and overburden materials to corroborate past laboratory and geochemical modeling predictions. We will also perform any ongoing or additional laboratory work that is needed to facilitate the comparison of modeling and field data.

REPORTS ISSUED DURING THE QUARTER

Peterson, S.R., A.R. Felmy, R.J. Serne, and G.W. Gee. 1983. Predictive Geochemical Modeling of Interactions Between Uranium Mill Tailings Solutions and Sediments in a Flow-Through System. NUREG/CR-3404, Nuclear Regulatory Commission, Washington, D. C.

REFERENCES

Balistrieri, L.S. and J.W. Murray. 1982. "The Adsorption of Cu, Pb, Zn, and Cd on Goethite from Major Ion Seawater." Geochimica et Cosmochimica Acta, 46:1253-1265.

Davis, J.A. and J.O. Leckie. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface: II. Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions." J. Colloid Interface Sci., 67:90-107.

Deutsch, W. J., E. A. Jenne, and K. M. Krupka. 1982. "Solubility Equilibria in Basalt Aquifers: The Columbia Plateau, Eastern Washington, U.S.A." Chemical Geology 36:15-34.

Gang, M. W., and D. Langmuir. 1974. "Controls on Heavy Metals in Surface and Ground Waters Affected by Coal Mine Drainage: Clarion River-Redbank Creek Watershed, Pennsylvania." In Proceedings of Fifth Symposium on Mine Drainage Research, pp. 3963. Coal and the Environment Technical Conference, October 22-24, 1974.

Hohl, H. and W. Stumm. 1976. "Interaction of Pb^{2+} with Hydrous $\gamma-Al_2O_3$." Journal of Colloid and Interface Science 55(2):281-288.

Jenne, E. A., J. W. Ball, J. M. Burchard, D. V. Vivit, and J. H. Parks. 1980. "Geochemical Modeling: Apparent Solubility Controls on Ba, Zn, Cd, Pb, and F in Waters of the Missouri Tri-State Mining Area." In Trace Substances in Environmental Health-XIV, D. D. Hemphill, ed., University of Missouri.

Leckie, J. O., M. M. Benjamin, K. Hayes, G. Kaufman, and S. Altman. 1980. Adsorption/Coprecipitation of Trace Elements From Water With Iron Oxyhydroxide. EPRI CS-1513 Project 910-1. Electric Power Research Institute, Palo Alto, California.

Nordstrom, D. K., E. A. Jenne, and J. W. Ball. 1979. "Redox Equilibria of Iron in Acid Mine Waters." In Chemical Modeling In Aqueous Systems. E. A. Jenne (ed.), ACS Symposium Series No. 93:51-79.

Peterson, S. R., and K. M. Krupka. 1981. "Contact of Clay Liner Materials with Acidic Tailings Solution. II. Geochemical Modeling." In Uranium Mill Tailings Management, Proceedings of the Fourth Symposium on Uranium Mill Tailings Management, Colorado State University, Fort Collins, Colorado, pp. 609-626, October 26-27.

Peterson, S. R., R. L. Erikson, and G. W. Gee. 1982. The Long-Term Stability of Earthen Materials in Contact with Acidic Tailings Solutions. NUREG/CR-2946 (PNL-4463), Nuclear Regulatory Commission, Washington, D. C.

METHODS OF MINIMIZING GROUND-WATER CONTAMINATION
FROM IN SITU LEACH URANIUM MINING

Project Manager: W. J. Deutsch
Principal Investigators: W. J. Deutsch and R. J. Serne
Support Investigators: A. R. Felmy, W. J. Martin, and B. Sass

FIN B-2379

OBJECTIVE

In this study we evaluate in situ uranium mining operations and restoration procedures and provide information to help NRC establish regulatory guidelines for the environmentally sound operation and abandonment of these mines. We evaluate existing production/restoration procedures and assess the potential for deleterious hydrogeochemical alterations resulting from lixiviant excursions and ore-zone mining.

ACCOMPLISHMENTS DURING THE PAST QUARTER

Task 1. Project Management

During the past quarter a schedule of work for FY-84 was developed and submitted to NRC as a revised Schedule 189 for this project. The primary emphasis of work in the coming year will be to: 1) complete field work in Wyoming and laboratory experiments on Wyoming sediments, 2) evaluate the ability of chemical reductants to enhance restoration, and 3) survey leach mine operators to evaluate the effectiveness of surface treatment techniques for aquifer restoration. A final report for the project will be written at the end of the fiscal year. Because of the expected lack of funding for studies of aquifer restoration in FY-85, the task to develop a plan and schedule for monitoring restoration at an in situ leach facility has been eliminated from the current version of the Schedule 189.

The document, Ground-Water Restoration Requirements, Techniques, and Practices at In Situ Leach Uranium Mines, (NUREG/CR-3104, PNL-4583) by W. J. Deutsch, N. E. Bell, B. W. Mercer, R. J. Serne, and D. R. Tweeton was sent to NRC for publishing. Some revisions in the document may be necessary before publishing to update certain sections of the report.

The paper by W. J. Deutsch and R. J. Serne on "Uranium Mobility in the Natural Environment: Evidence from Sedimentary Roll-Front Deposits," (PNL-SA-1075) was presented at the International Symposium on the Geochemical Behavior of Disposed Radioactive Waste in Seattle during March, 1983, and has been submitted to the sponsors of the symposium for publication. The paper will appear as an article in the American Chemical Society Symposium Series.

Task 2. Site Characterization

It was decided at the February NRC review of this project that a site should be chosen in Wyoming where samples of ground water and sediment could be obtained from an aquifer containing a roll-front uranium ore deposit. Coring at a current drilling site near Douglas, Wyoming, was site was carried out during August. Four coreholes were drilled from which approximately 30 ft of reduced sediment, 10 ft of ore, and 7 ft of oxidized sediment were recovered. The sediment was stored in PVC tubes that were evacuated with argon to inhibit oxidation of the sediment during storage. The samples were returned to PNL where they will be characterized and used in future laboratory experiments on natural and induced restoration. Samples of ground water from monitor wells at the Wyoming pilot plant will be taken in October to complete the characterization of this Wyoming roll front and provide data on the Wyoming deposit that can be compared with data on the Texas deposit.

Task 3. Natural Restoration Processes

The batch experiment in which leached ore and reduced sediment from the leach mine were reacted with lixiviant was completed during the past quarter. The results of the experiment will be described in detail in the letter progress report in November. A summary of the experiment follows.

The objective of the batch experiment was to determine the sequence of reactions and the outcome of storing lixiviant in contact with aquifer sediments for a relatively long period of time (up to 3 months). In the batch experiment, containers of leached ore and lixiviant and reduced sediment and lixiviant were sealed to prevent oxygen contamination and stored for a set period of time. There was a total of 28 samples; 14 for each sediment type. Samples of solution from the containers were taken after 2, 4, 8, 16, 36, 75, and 101 days of contact time. At each sampling time two containers of each sediment type were used to provide solution samples. The solutions were analyzed for most major, minor, and trace inorganic constituents. Changes in solution concentration of calcium, sulfate, iron, and uranium over the period of solution/sediment contact were significant and provide important information on the probable reactions in the system.

When the lixiviant was added to the leached ore and the reduced sediment, the amount of calcium dissolved in the solution increased from 200 mg/l to approximately 500 mg/l and sulfate increased from 1320 mg/l to approximately 2300 mg/l. The higher concentrations are what would be expected if gypsum were dissolving from the sediment and equilibrating between the solution and sediment. Gypsum is not a normal component of the aquifer sediments, and we believe that it was produced in the leached ore by oxidation of pyrite during the leaching process. Gypsum may have been produced in the reduced sediment by pyrite oxidation during collection and storage of the sample.

The iron concentrations for the leached ore samples show a rapid and large increase at the beginning of the experiment and level off between 16

and 36 days at approximately 27 parts per million (ppm) (Figure 1). The concentration of dissolved iron for the reduced sediment samples shows an increase after 16 days of the experiment, but the maximum value achieved is only 3.9 ppm (Figure 1). In samples from 75 and 101 days, the iron values have decreased for both sediment types and reach lows in the range of 0.1 to 3 ppm with the leached ore samples having the higher concentrations. Preliminary interpretation of the behavior of iron during the experiment is based on the solubility of ferric hydroxide in low redox potential solutions and the precipitation of ferrous sulfide minerals. Ferric hydroxide is present in the leached ore as a by-product of the leaching process, and it is present in the reduced sediment because the sample is unavoidably exposed to oxygen in the atmosphere during sample collection. Redox reactions during the batch experiment produce reducing conditions relative to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. Under these conditions, ferric hydroxide is unstable and dissolves, which provides for the increase in dissolved iron as Fe(II) during the experiment. More dissolved iron is present in the leached ore batch samples because more ferric hydroxide was originally present. Continued redox reactions produce conditions in which dissolved sulfide is generated. Ferrous sulfide minerals are relatively insoluble and their precipitation removes iron from solution lowering the total iron concentration as seen in Figure 1 for the 75-day and 101-day samples.

Adsorption and mineral precipitation probably caused changes in uranium concentration during the experiment. The uranium concentration in the lixiviant used for the batch experiment is 52 mg/l. On addition of the lixiviant to both sediment types, the solution concentration of uranium dropped to approximately 20 mg/l. This is believed to result from adsorption of the uranium onto the sediment. Under the oxidizing conditions that existed at the beginning of the experiment, a uranium concentration of 20 mg/l is well below the solubility of any uranium mineral that might form in this system. As contact time increased and the redox potential of the solution was lowered, the dissolved uranium concentration decreases. After 101 days of contact the uranium concentration in solution associated with both the leached ore and reduced sediment was less than 1 mg/l. This decrease in dissolved uranium concentration is probably due to the reduction of U(VI) to U(IV) and the precipitation of a uranium mineral under the reducing conditions. Removal of uranium from solution by natural processes will produce a stable uranium equilibrium between the solution and the sediment and will enhance induced restoration.

Task 4. Induced Restoration Techniques

During the past quarter, chemical addition techniques have been studied as a method of in situ restoration and stabilization of the leached zone. Theoretical calculations based on available thermodynamic data were used to predict dominant uranium complexes in solution and to determine the chemical properties of several sulfur-based reductants. Quantitative calculations have been made to determine the amount of a given chemical agent required for reduction of mobile hexavalent uranium to tetravalent species which can form stable solids. A series of experiments were conducted to test the effect of chemical reductants on the composition of the pregnant lixiviant collected from the leached mine.

The choice of a reductant to be used for aquifer restoration should be based on effectiveness, cost of materials and equipment, safety, and environmental factors. Sodium sulfide, sodium sulfite, and hydrogen sulfide gas are being evaluated with these factors in mind. While all three reductants were determined to be equally effective in removing 10 mg/l of uranium and 10 mg/l of oxygen from solution, their individual costs to treat an aquifer increase from hydrogen sulfide (\$21 per million gallons treated) to sodium sulfide (\$102 per million gallons) and sodium sulfite (\$150 per million gallons). However, the cost of even the most expensive reductant may be economical compared to other restoration techniques if a redox-sensitive element is a major contaminant in solution.

Products and byproducts of the reductants may have both adverse and beneficial effects on restoration. For example, using sodium sulfide and sulfite will increase dissolved sodium in the ground water by 31 mg/l (if 10 mg/l of oxygen and uranium are reduced). The increase in sodium concentration may deflocculate smectite clays which may decrease the permeability of the aquifer. The reduced sulfur species added as a reductant will produce sulfate upon oxidation, and this will increase sulfate concentration in the water. The reestablishment of reducing conditions in the leached zone may cause the dissolution of ferric hydroxide minerals (as was found in the batch experiment with leached ore). Iron concentrations will increase in solution unless reductants such as sodium sulfide or hydrogen sulfide are used. The dissolved sulfide will react with the iron in solution to form ferrous sulfide minerals which are not very soluble under reducing conditions. Furthermore, oxidation of sodium sulfide and hydrogen sulfide produces S(0) which is believed to be necessary in the process of crystallizing pyrite and marcasite from less stable iron sulfides; (e.g., amorphous FeS). Pyrite is the most insoluble form of iron sulfide, hence the most desirable ferrous mineral in the aquifer. Also, pyrite is generally present in unleached ore and it provides some of the reducing capacity for the natural aquifer system. The regeneration of pyrite during restoration would be a significant contribution toward returning the aquifer to its pre-mining chemical state.

Laboratory experiments were conducted to determine the effects of adding hydrogen sulfide and sodium sulfite to a lixiviant. Lixiviant which had been bubbled with hydrogen sulfide exhibited decreases in pH (from 8.0 to 6.1), Eh (from +0.3V to -0.26V), and uranium concentration from 42 mg/l to less than 1 mg/l. Tests with sodium sulfite added to lixiviant did not show the expected changes in solution parameters. Reducing conditions were not established and uranium concentration was not lowered appreciably. We believe the problem with the sodium sulfite test was contamination with atmospheric oxygen; future tests will be designed to eliminate this problem.

HIGHLIGHT CONCLUSIONS

Sediment samples were collected from a Wyoming roll-front uranium deposit. The sediments will be used to characterize the geochemistry of a typical

chemical environment and that of the Texas site sampled last year. Also, the sediments will be used in laboratory experiments to evaluate restoration methods.

A batch experiment with the Texas aquifer sediments and lixiviant was completed this quarter. It showed that undisturbed contact of the solution and sediment can lead to a series of reactions that might temporally increase iron concentrations in solution to above baseline levels, but will ultimately lower the redox potential of the solution leading to low dissolved iron and uranium concentrations.

Theoretical calculations showed that sulfur-bearing reductants will effectively lower oxygen concentration in spent lixiviant and will decrease the redox potential to the point that uranium and other redox-sensitive contaminants will be removed from solution by mineral precipitation. Sulfide will also combine with any ferrous iron released during the process of reducing the aquifer to form relatively insoluble minerals that will limit the dissolved iron concentration to below contaminant levels.

PROJECTED WORK FOR NEXT QUARTER

Ground water samples will be collected up and down the hydrologic gradient from a Wyoming roll-front uranium deposit to complete site characterization work in Wyoming and provide solutions for laboratory experiments. A laboratory experiment designed to simulate ground-water sweeping will be conducted. We will continue both the theoretical and laboratory evaluation of the effectiveness of various chemical reductants. A letter progress report that documents our current work on natural and induced restoration will be submitted during November.

REPORTS ISSUED DURING QUARTER

None.

FIGURE 1. Iron Concentrations in Solutions from the May-February, 1983 Batch Experiment.

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