Waste/Rock Interaction Technology Program

**Proceedings of the Task 2
Workshop
Waste Isolation Safety
Assessment Program**

MASTER

Don J. Bradley, Chairman

Seattle, Washington
24-25 May 1979

Prepared for
Office of Nuclear Waste Isolation
under its Contract with the
U.S. Department of Energy

Pacific Northwest Laboratory
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by Battelle Memorial Institute

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Waste/Rock Interaction Technology Program

PROCEEDINGS OF THE TASK 2 WORKSHOP
WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

D. J. Bradley, Chairman

Seattle, Washington
24-25 May 1979

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On 1 October 1979, WISAP became the Assessment of Effectiveness of Geologic Isolation Systems (AEGIS) program and the Waste/Rock Interaction Technology (WRIT) program. This report is issued by WRIT.

We wish to thank Jody Marshall of Battelle-Seattle and her staff for making the arrangements for the conference and who organized the lodging, food, and audiovisual services.

We are grateful to the Office of Nuclear Waste Isolation for their monetary support and technical assistance.

The effort of all the attendees, scheduled and informal speakers who generated discussion and ideas on program guidance is much appreciated.

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SUMMARY

The workshop on Waste Form Release Rate Analysis brought together experts in waste form leaching and surface science analysis to review the work done to date and to exchange ideas on the direction of future work.

This program is directing its efforts toward experimental determination of how nuclear waste forms perform in a geologic repository. The data on, and mechanistic understanding of nuclide release, will be used for release consequence analysis and radionuclide migration studies.

In addition to those directly involved with this program, specialists from similar or related programs attended the workshop to provide comments and describe the status of their work. The workshop started with overview presentations on:

- The Office of Nuclear Waste Isolation (ONWI),
- The Waste Isolation Safety Assessment Program (WISAP),
- WISAP Task 2, Waste Form Release Rate Analysis,
- WISAP Task 4, Sorption/Desorption Analysis.

Technical presentations followed concerning these areas:

- leaching studies on spent fuel,
- leaching studies on high-level waste glass,
- waste form surface science experiments,
- radiation effects,
- leach modeling.

After the formal presentations an open-floor discussion was held to get comments on program direction. The major comment concerned work on spent fuel. More funding is needed to accelerate testing of spent fuel. In general, work is needed on tests that integrate together the waste package "system," the waste form, canister, engineered barrier and backfill, and surrounding host rock. Although these tests are expected to be expensive, they are necessary since they will provide the data base for models describing repository safety. Without this data base support, the models have limited credibility and may not survive the licensing process.

It was also concluded that the leaching model, as a working hypothesis without ignoring the complexities of the reactions involved, and a data bank should be emphasized in the future.

Since this workshop had representatives from different laboratories, some of the terminology varied. For the sake of uniformity, we will use the term "Exhibit" in place of the words: figure, slide, vu-graph, and table. Exhibits will follow the text in each section.

FOREWORD

The Waste Isolation Safety Assessment Program (WISAP) has the objective of obtaining scientifically defensible generic and site specific data along with modeling methodology to be used to assess the safety of geologic disposal of nuclear waste. Within this objective, Task 2 of the WISAP program is charged with obtaining radionuclide release rates and understanding the release processes from candidate waste forms under simulated geologic storage conditions. This information will be used to develop a data bank and a release model for input to the release consequence task of WISAP.

The workshop had the following objectives:

- Provide an overview of the ONWI and WISAP programs to show how the work being done will be utilized.
- Discuss the WISAP Task 2 program goals and methodology.
- Review all the work being done for WISAP Task 2, both at PNL and the subcontractors.
- Encourage discussion concerning the work to date and directions of future work.

Those attending represent the key personnel from PNL and subcontracting laboratories. Also attending were representatives from the Office of Nuclear Waste Isolation, U.S. Geologic Survey, the Atomic Energy of Canada, Sandia Labs, and Los Alamos Scientific Laboratory that are conducting similar work or have high interest in this area.

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WISAP TASK 2 WORKSHOP

Attendees

<u>Affiliation</u>	<u>Name</u>
Argonne National Laboratory	H. Diamond
	A. Friedman
	D. Lam
Atomic Energy of Canada	G. Strathdee
Battelle-Pacific Northwest Laboratory	J. Jarrett
Battelle-Pacific Northwest Laboratory	D. Bradley
WISAP Task 2	C. Harvey
	B. Katayama
	G. McVay
	J. Mendel
	L. Pedersen
	J. Swanson
	M. Thomas
	R. Turcotte
	J. Westsik, Jr.
Battelle-Pacific Northwest Laboratory	J. Serne
WISAP Task 4	
Battelle-Pacific Northwest Laboratory	A. Brandstetter
WISAP	B. Howes
Brookhaven National Laboratory	P. Colombo
	R. Neilson, Jr.
Lawrence Livermore Laboratory	D. Coles
	J. Tewhey
	H. Weed
Los Alamos Scientific Laboratory	E. Norris
Office of Nuclear Waste Isolation	J. Kircher
Sandia Laboratories	M. Molecke
U.S. Geologic Survey	D. Stewart (Reston, VA)
	A. White (Denver, CO)

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WISAP 2 WORKSHOP

May 24-25, 1979

May 24, 1979

Agenda

8:00 am	Registration (Seminar Lobby)	
8:30 am	Welcome Notes on schedule Announcements	D. Bradley
8:45 am	ONWI Program	J. Kircher
9:00 am	WISAP Overview	A. Brandstetter
9:20 am	WISAP Overview Task Structure	D. Bradley
10:10 am	Coffee Break	
10:25 am	WISAP 4 Overview	R. Serne
10:45 am	Non-Flow Release Studies	D. Bradley
11:10 am	Autoclave Studies	J. Westsik
11:40 am	Release Model Development	R. Turcotte
12:00 noon	Lunch	
1:00 pm	Gamma Field Experiment	G. McVay
1:40 pm	Continuous Flow Studies	D. Coles/H. Weed
2:15 pm	Transuranic Studies-BNL	P. Colombo/R. Neilson

2:50 pm	Surface Studies-PNL	M. Thomas
3:30 pm	Break	
3:45 pm	Surface Studies-ANL	B. Lam
4:15 pm	Anoxic Leach Test-ANL	H. Diamond
5:15-6:15 pm	Social Hour (Lounge)	

May 25, 1979

8:00 am	Spent Fuel Studies-PNL	Y. Katayama
8:40 am	Spent Fuel Studies-Canada	G. Strathdee
9:20 am	WIPP Overview and TRU/HLW Work	M. Molecke
10:00 am	Break	
10:15 am	The Approach to Understanding Waste Rock Interactions and Long-Term Prediction	All
	Lead Off: J. Mendel D. Stewart	
12:00 noon	Lunch	
1:00-4:00 pm	Continuing Discussion	

OVERVIEW OF THE OFFICE OF NUCLEAR WASTE ISOLATION

by

J. F. Kircher

For some years there has been a general belief in the scientific community that the extreme isolation, with minimal surveillance and maintenance, considered desirable for High Level Waste (HLW) and Transuranic (TRU) wastes can be found in deep, stable geologic formations. Many such formations apparently have been stable for millions of years, giving reason to believe that wastes placed within them with suitable care will remain in isolation for similar geologic periods.

The U.S. Department of Energy (DOE) has the responsibility to provide geologic repositories and associated facilities for the long-term storage and disposal of radioactive wastes from DOE facilities and from commercial facilities. Such repositories must offer safe, environmentally acceptable storage for:

- Spent unprocessed reactor fuel
- Solidified HLW from reprocessing operations, should they be conducted
- Other commercial nuclear waste, as appropriate
- HLW or other waste from defense sites, as appropriate.

These repositories would be operated for a period of time in such a manner that HLW or spent fuel could be retrieved, if necessary. After full demonstration of a repository as a terminal isolation facility, it would be used for nonretrievable isolation of these and other waste materials.

DOE is sponsoring research projects to investigate the feasibility of constructing repositories in several different geological systems as consistent with the Interagency Review Group (IRG) recommendations. Heavy emphasis is to be placed on the development of an adequate technology base to support design and licensing activities. Many agencies and commercial organizations

are involved in this work. The Office of Nuclear Waste Management (ONWM), which reports directly to the Assistant Secretary, Energy Technology, has overall responsibility for the DOE waste management program. Although there is much overlap in use of facilities and exchange of technology, this program, in general, is focused on two separate areas: commercial waste management and defense waste management.

The DOE Commercial Waste Management Program involves the following:

- Development of isolation technology
- Repository siting, a process based upon geologic factors, National Environmental Policy Administration (NEPA) compliance, economic factors, and development of a National consensus on waste isolation
- Facility design and development
- Development of technology for any prerequisite treatment and packaging of waste.

The Commercial Waste Management Program is managed in the field, primarily by the DOE Richland Operations Office (RL), which oversees the National Waste Terminal Storage Program (NWTs). On July 1, 1978, Battelle Memorial Institute, Columbus, Ohio, under contract to DOE, which is administered by RL, established the Office of Nuclear Waste Isolation (ONWI) to assume management and coordinating functions in connection with the NWTs program. Previously the Office of Waste Isolation (OWI), operated by Union Carbide Nuclear Division at Oak Ridge, Tennessee, had similar responsibilities. ONWI interfaces with RL and DOE through the National Waste Terminal Storage Program Office (RL-C) in Columbus.

ONWI is responsible for the overall direction and coordination of the technology programs supporting the NWTs effort. In this role, ONWI has responsibility for generic research and development which will provide data common to a wide range of possible repository sites and designs. Specifically, ONWI's responsibilities include systems analysis, site qualification criteria, methods development, standards development, and licensing methodology and data. ONWI will also provide support to specific project needs of the Waste

Isolation Pilot Plant (WIPP), Basalt, and Nevada Nuclear Storage Investigation (NNSI) programs, as appropriate. The WIPP, Basalt, and NNSI programs are responsible directly to DOE for adherence to project cost, schedule, and technical objectives, but are developing information of interest in the NWTs program. The intent of the ONWI coordination function is to reduce duplication of effort and increase the consistency of the technical approach and data.

In addition to its role in the NWTs program, ONWI supports the DOE public information program on waste isolation efforts, and also provides, upon request, direct support to DOE Headquarters by undertaking special studies, evaluating proposals, developing new concepts, and coordinating technical programs.

ONWI is a project management organization. All research associated with the program will be carried out by qualified subcontractors, some of whom will be given coordinating responsibilities. Exhibit 1 shows the organization of the Office of Nuclear Waste Isolation.

The overall goal of the NWTs program is to identify and/or develop technology that will provide a high degree of assurance that existing and future high-level nuclear wastes (HLW) produced from Government and Commercial activities can be isolated from the biosphere in a safe, environmentally acceptable manner. ONWI was established by DOE to address specific work elements within the NWTs program. ONWI's specific objectives are twofold:

- 1) To identify and characterize geologic sites for use as nuclear waste repositories
- 2) To manage the development and application of specific supporting data and base technologies.

These relatively broad objectives are the motivation of the activities ONWI conducts in addressing its responsibility to DOE for the overall direction and coordination of research and development programs associated with the NWTs effort, in supporting the DOE public information program on waste management, and in providing special technical studies for DOE Headquarters. The scope of these activities is defined as:

ONWI is "... to provide management and technical direction to the National Waste Terminal Storage program consistent with the guidance provided by DOE. To the maximum extent practicable, actual performance of the work is to be performed by organizations with expertise applicable to fields of technology under contract to ONWI and/or other DOE contractors. ONWI's management effort under this program shall consist of, but not be limited to, the following areas:

- Site and Repository Development - Identification of potential sites in salt or other geological formations within the United States suitable for development as potential terminal waste repositories. This shall include management efforts related to qualification of the sites to comply with specific licensing criteria set forth by DOE and the Nuclear Regulatory Commission (NRC). In addition, direction of activities in support of design, construction, licensing, and operation of these repositories is within the scope of work.
- Technology Development - Identification, coordination, and direction of the development of the criteria and specific technologies required for the exploration, design, licensing, construction, operations, decommissioning, and monitoring of the nuclear waste repositories. These activities include a strong basic science program for development of the extensive data bases required for an understanding of general phenomena, geological processes, and all other interrelated factors associated with the disposal of nuclear wastes in a safe manner."

The ONWI Work Breakdown Structure (Exhibit 2) defines specific elements of work derived from the above scope. These have been organized into a comprehensive research program directed toward the achievement of specific objectives and milestones established by DOE within the context of the two general objectives stated above.

Exhibit 3 shows a breakdown of the Technologies Development and Application function of ONWI.

To address the need to develop the methods, generic data, and analyses that are necessary for predicting the long-term safety of geologic isolation repository systems, work is continuing on the Waste Isolation Safety Assessment Program (WISAP), sponsored by ONWI and managed within the Technology Development Department under W. A. Carbiener. The results of this

major project will be applied to site qualification and repository performance assessment, and its development involves four tasks:

- 1) Release scenario analysis. Potential natural or man-caused events that could conceivably compromise the integrity of a geologic containment medium and lead to accelerated nuclide leaching are being analyzed.
- 2) Waste form release rate data development. Laboratory work is being directed toward determining the radioactive composition and release rate of leach products that would emanate from a waste form were it exposed to groundwater as a consequence of a breach in the geologic isolation barrier.
- 3) Release consequence analysis. Presently available hydrologic, geosphere transport, and biosphere transport models will be adapted and/or extended to provide a method to estimate the consequences of potential accidental releases of radioactivity from a repository, primarily through groundwater intrusion.
- 4) Sorption/desorption studies. Laboratory work will be directed toward determining nuclide transport factors in various host media (salt, shale, granite, etc.), and with various groundwaters, over a range of temperature and pressure.

This workshop is concerned with WISAP Task 2 which will evaluate the performance of waste forms under geologic storage conditions and provide data for the source term required for release consequence analysis.

Data pertinent to thermal, mechanical, and compositional properties of candidate waste forms are being generated in other DOE programs that are developing solid waste forms. It is likely that minimal additional experimental work will be required beyond that being developed in these several programs, although the existing data will need to be assembled and collated for use in performance and safety analyses.

Laboratory test programs are being conducted by WISAP Task 2 to determine leach rates and leachate compositions as a function of waste chemical composition, immobilizing phases, and hydrothermal conditions. Reactions with various candidate host rocks, groundwaters, and engineered barriers (as developed)

are being investigated, including mechanism studies to enhance predictive capabilities.

Although currently available leach rate data is still somewhat sparse, particularly for spent fuel, Task 2 and other data sources are providing preliminary source term inputs now to those doing consequence analysis. As the NWTS program moves closer to site qualification in several geologies and toward the licensing process, the demand for waste form stability data in a variety of geologic environments will certainly increase.

EXHIBIT 1. Organization of the Office of Nuclear Waste Isolation (ONWI)

EXHIBIT 2. ONWI Work Breakdown Structure

EXHIBIT 3. ONWI Technologies Development and Application Breakdown

THE WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

by

A. Brandstetter

Associated with commercial nuclear power production in the United States is the generation of potentially hazardous radioactive wastes. The Department of Energy (DOE), through the National Waste Terminal Storage (NWTs) Program, is seeking to develop nuclear waste isolation systems in geologic formations that will preclude contact with the biosphere of waste radionuclides in concentrations which are sufficient to cause deleterious impact on humans or their environments. Comprehensive analyses of specific isolation systems are needed to assess the expectations of meeting that objective. The Waste Isolation Safety Assessment Program (WISAP) has been established at the Pacific Northwest Laboratory (operated by Battelle Memorial Institute) for developing the capability of making those analyses.

Among the analyses required for isolation system evaluation is the detailed assessment of the post-closure performance of nuclear waste repositories in geologic formations. This assessment is essential, since it is concerned with aspects of the nuclear power program which previously have not been addressed. Specifically, the nature of the isolation systems (e.g., involving breach scenarios and transport through the geosphere), and the time-scales necessary for isolation, dictate the development, demonstration and application of novel assessment capabilities. The assessment methodology needs to be thorough, flexible, objective, and scientifically defensible. Further, the data utilized must be accurate, documented, reproducible, and based on sound scientific principles.

INTRODUCTION

The objectives of the Waste Isolation Safety Assessment Program (WISAP) are to: 1) develop the capabilities needed to assess the post-closure safety of geologic repositories, 2) obtain scientifically defensible generic and site-specific data necessary for safety assessments, 3) provide, as needed,

studies to further support these data and analyses, 4) demonstrate the assessment capabilities by performing analyses of reference sites, 5) apply the assessment methodology to assist the National Waste Terminal Storage Program in site selection, and 6) perform repository site analyses responsive to the time schedule and to the level of sophistication required to meet the licensing needs of the National Waste Terminal Storage Program.

Post-closure safety assessments will be required at differing levels of detail as the repository site selection, qualification, and licensing processes develop. Thus, the safety assessment program needs to continue to evolve to match the technical detail and sophistication of the assessment input required by the various site qualification and licensing stages.

In summary, a post-closure safety assessment program must advance the state-of-the-art for assessment capabilities while providing, in a timely manner, the credible assessments required to evaluate specific geologic isolation systems.

There are two basic components of repository post-closure safety assessments:

- identification and analyses of breach scenarios and the pattern of events and processes causing each breach;
- identification and analyses of the environmental consequences of radionuclide transport and interactions subsequent to a repository breach.

The current scope of the WISAP is limited to long-term, post-closure analyses. It excludes the consideration of processes that are induced by the presence of the wastes that may affect the repository integrity, and it excludes the consideration of nuclear waste isolation other than geologic isolation repositories. The near-field/near-term aspects of geologic repositories are being considered by ONWI/DOE under separate programs. They will be integrated with the WISAP methodology for the actual site-specific repository safety analyses.

The Waste Isolation Safety Assessment Program is divided into a management task and four technical tasks (Exhibit 1). These tasks are designed to be integrated to produce the needed assessment methodology and site analyses. These tasks, involving the Pacific Northwest Laboratory and subcontractors are described below.

EXHIBIT 1. WISAP Task Interrelationships

RELEASE SCENARIO ANALYSIS

Task 1, Release Scenario Analysis, utilizes geoscientist teams and mathematical models to identify and predict the events and processes which could potentially affect the repository integrity. This includes the analysis of the interactions and sequences of phenomena which could result in a loss of containment by the repository. Based upon the particular nature of a release sequence of phenomena, the condition of the geology surrounding the repository at the time of the breach will be determined as initial conditions for the consequence analysis.

Thus, the functions of Task 1 are to:

- specify possible release scenarios;
- identify the sequence of events and processes which could lead to such scenarios;
- describe the state of the surrounding geology as initial conditions for consequence analyses.

The purpose of this task is to analyze nuclear waste repository release scenarios. Task 1 considers geologic events and processes, man-caused events and processes, and the impact of these on the integrity of the repository. Events, such as earthquakes, faulting and human-intrusion, and processes, such as erosion, uplift and diapirism, could alone or in concert significantly alter the geology surrounding the repository, leading to a loss of repository integrity. The output from this task will establish the conditions of the geology and hydrology surrounding the repository at the time of an identified breach. Thus, Task 1 will provide the major geologic boundary conditions for input into the consequence analysis models of Task 3.

Development of the release scenario analytical capability is being performed in a two-stage approach. This year, an ad hoc team of geoscientists is generating release scenarios for reference sites as inputs from Task 1 to Task 3. Concurrently, release scenario models are being developed so that in subsequent years the models can be utilized to assist in the generation of

release scenarios. These two approaches are intimately interrelated, so that the information and data developed from the effort of the geoscientists are being used to aid in the conceptualization of the differing geologic parameters incorporated in the developing models. Conversely, the expert team efforts are utilizing the intermediate stages of the models being developed to aid, insofar as possible, in focusing the scenario generation.

This task has essentially completed the initial, generic phase of work. This phase involved:

- survey of possibly applicable methodologies and selection of the release scenario methodology to be used for site scenario analyses;
- publication of a scenario analysis methodology report;
- identification of potentially disruptive events and processes;
- completion of initial consultant efforts to characterize and quantify the identified potentially disruptive phenomena;
- receipt of all 1978 consultant reports and initiation of synthesis of these for the scenario methodology development.

Completion of this initial, generic phase allows the transition of Task 1 efforts to the development of geologic-specific and site-specific release scenario methodology.

Specifically, the generic phase has provided the baseline from which actual release scenarios for reference site initial analyses are being generated this year. Also, the development and testing of the generic computer program during the initial phase of Task 1 formed the basis for the development of geologic-specific, second generation models. Thus, while sophisticated scenario models will not be available for site applications this year, prerequisite steps have been completed which will simultaneously allow ad hoc team utilization of WISAP technology for site scenario analyses and continuation of release scenario model development.

The thrust of Task 1 this year is to provide geoscientist-generated scenario inputs to Task 3 for reference site initial assessments, and to continue

development of scenario models which will be utilized next year for site assessments.

WASTE FORM RELEASE RATE ANALYSIS

Task 2, Waste Form Release Rate Analysis, is investigating leaching rates and processes of radionuclide release from nuclear waste forms, providing essential source terms for radionuclide movement. These rates are of major importance to breach consequences because slower leach rates add time delays prior to the hydrologic transport of the radionuclide inventory. Such delays can be important factors in containment, especially for radionuclides of rapid or intermediate decay rates. Leach rates are dependent upon the characteristics of the waste forms and the extant physicochemical conditions within the repository at the time of breach.

A more detailed discussion of Task 2 will be presented following this report.

RELEASE CONSEQUENCE ANALYSIS

Task 3, Release Consequence Analysis, is utilizing groundwater and radionuclide migration models to simulate the pathways and transit times of each radionuclide to the biosphere, assuming that radionuclide geosphere transport would be primarily by water. For radionuclides reaching the surface, radiological dose models are used to compute exposures to humans and their environment. Thus, the functions of Task 3 are to:

- provide simulations of water movement through the geosphere from the repository proximity;
- provide simulations of the transport of radionuclides through the geosphere, driven by the water flow;
- provide source terms for the radiological dose models;
- predict anticipated radiological dose levels for humans and their environment based on the geosphere simulations.

The purpose of this task is to provide the capability for analysis of radiological consequences of a repository breach. This includes analysis of the transport of radionuclides from the repository proximity to the biosphere and computation of the individual and population doses resultant from the biosphere entry.

It is assumed that the movement of radionuclides through the geosphere would be primarily by water transport. Thus, the geosphere transport aspect of this task has two components: 1) the identification, through simulation, of the potential water pathways and transit times, and 2) the juxtapositioning of the actual radionuclide movement onto this hydrologic regime, taking into consideration factors affecting chain decay and transport. Added onto the output of these geosphere models are radiological dose models, so that three model sets are involved in this task. Additionally, within each model grouping are models of differing levels of complexity, so that the degree of model sophistication can be attuned to the adequacy of the data base for each particular analysis, and to the purpose of the analysis (e.g., preliminary planning, site selection, licensing of specific site). Thus, Task 3 currently provides a flexible capability for consequence analysis.

This year, a major objective of this task is to utilize these extant models to perform reference site initial analyses for several differing geologies, including domed salt, bedded salt, and basalt sites. This effort will enhance the model development effort. The objectives are to increase the efficiency, defensibility, and credibility of the models so that later more complete site-specific analyses can be performed to the depth required for the licensing process. Finally, Task 3 is a focal point for data base collation, both from within and from outside WISAP.

Task 3 efforts to date have brought that task to the point where actual site-specific analyses can now be made. A synopsis of the Task 3 status includes:

- The data base system has been established on a flexible data retrieval system. Generic data have been compiled for test case model runs and

verification. Site-specific data for a bedded salt site have been added to the system.

- The hydrologic models selected for WISAP use (VTT, 3-d F.E., PATHS) have been implemented, sensitivity analyses have been performed, and test cases have been run for verification.
- The radionuclide transport models selected for WISAP use (GETOUT, MMT) have been implemented, sensitivity analyses have been performed, and test cases have been run for verification.
- Previously developed radiological dose models have been converted to the Univac 1100/44 computer system and are fully operational.
- A test case of the release consequence analysis methodology has been completed to exercise the Task 3 models and their interfaces. Results indicate Task 3 models can now be utilized for initial assessments of site-specific cases, subject to availability of the necessary data and release scenarios.

SORPTION/DESORPTION ANALYSIS

Task 4, Sorption/Desorption Analysis, is investigating radionuclide sorption processes. If radionuclides are actually released into a transporting groundwater, these may be sorbed by the geomedia which they contact. Irreversible sorption would act to remove the radionuclide from the water. Reversible sorption would act in a manner similar to waste form leaching, by providing time delays to the migration of radionuclides. Geomedia of sufficient sorptive capability could provide isolation of the waste from the biosphere by extending transit times to very long periods of time. As with leaching, sorption/desorption by geomedia is dependent upon the specific radionuclide involved and the physicochemical characteristics of the geomedia and transporting solutions. Task 4 will be discussed in greater detail later.

PROJECT MANAGEMENT

Providing overall management coordination to the four task efforts is the Management Task. The functions of this task are to:

- provide technical coordination across the four tasks;
- provide a centralized communication link with DOE and the Office of Nuclear Waste Isolation (ONWI);
- provide communications and coordination with site Geologic Project Managers (GPM) and Repository Project Managers (RPM);
- enhance interfaces of WISAP with other research and development efforts (e.g., near-field methodology, in-situ testing);
- implement the quality assurance (QA) program as specified by the WISAP QA Plan;
- provide fiscal project control and management;
- provide integration of WISAP efforts with requirements for site selection and licensing.

The project management task provides the coordination of the diverse activities among the technical tasks. To meet this objective, this task monitors each of the other tasks and continuously analyzes all ongoing WISAP activities with respect to their need. This task thus provides the integration of the overall WISAP effort with the requirements for site selection, qualification, and licensing. The management task also provides the integrative role of coordinating the activities of each of the technical tasks for the reference site initial assessment, including analyzing the task outputs and issuing the analyses reports.

This task is also performing systems analyses of WISAP methodology to guide future WISAP work and interfaces with other aspects of the National Waste Terminal Storage Program. These systems analyses are being performed to identify the important parameters and functions of the safety assessment system. Since the assessments which WISAP will provide for site qualification will vary in the degree of sophistication required, the management task will coordinate the WISAP efforts and plans vis a vis the licensing process, as that process becomes clarified.

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WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

TASK 2

WASTE FORM RELEASE RATE ANALYSIS

by

D. J. Bradley

The purpose of this task is to measure and understand radionuclide release rates for waste forms anticipated for geologic isolation. At the present time, these waste forms include spent fuel, High-Level Waste (HLW) glass, and for TRU, concrete, bitumen, urea-formaldehyde, and polymers. Radionuclide release processes are of major importance to breach consequence analyses because slower leach rates delay the transport of radionuclides from a breached repository to the biosphere. These processes are also responsible for determining the "source term" for migration away from the repository.

The limited amount of information on leach rates that is available ignores the specific effects of the canisters, backfill, geology, and hydrology. Also lacking is detailed information on the state of the nuclide once it has been released from the waste form. Nuclide valence state and chemical specied data is therefore needed. Task 2 is directing part of its efforts to determine this data so as to provide correct nuclide flux information for migration studies.

Exhibit 1 summarizes the objectives of WISAP Task 2. Exhibit 2 shows how WISAP Task 2 and its subcontractors are integrated with the overall WISAP program on the basis of data collection. Waste form analysis simply means the characterization of the sample prior to starting a leach test. This includes chemical and radionuclide composition, homogeneity, structure, crystalline phases present, and their composition and physical properties such as density and surface area. For spent fuel and waste glass this work is done at PNL; for TRU waste forms it is being done at Brookhaven National Laboratory.

All subcontractors are performing leach tests as indicated by Exhibit 2. This area also interfaces with WISAP Task 1, to obtain release scenario

information, and WISAP Task 4, to provide actual leachates for sorption studies. Information from both of these areas is incorporated into a data bank and, with interpretation (aided by detailed waste form surface and leachate solution analysis), produces a model to describe the release behavior observed. This area refers back to the Release Model Development subtask shown in Exhibit 3, which is the current structure of WISAP Task 2. Release rate tests and waste form analysis make up the remainder of the subtasks shown. Although each subtask will be discussed in detail during this workshop, Exhibits 4-8 outline the objectives for the subtasks.

The work of WISAP Task 2 can be broken down into three phases as indicated by Exhibit 9. The work described so far is the first phase. This work to date has been on the simple waste form-generic groundwater binary system. This will provide functional relationships between element release and laboratory time, temperature, solution composition, and solution flow rate. This information is needed in order to describe release in case all other barriers fail (such as a fault in the repository) and to provide a baseline for interpreting the more complex waste form alterations and mineralogic reactions that will occur in Phase II. Exhibit 10 outlines the objectives of Phase I.

The behavior of the waste, groundwater, canister, backfill, engineered barrier, and host rock system is the subject of the Phase II testing program. These integrated tests more accurately describe the real repository system and we must gain some understanding of the effect of this complex system on the degradation of the waste form, release of radioisotopes and their interactions with the immediate surroundings, the very near field zone. This is necessary if we hope to have any confidence in our safety assessment and radionuclide migration predictions.

It must be emphasized that detailed solid state and solution analysis be incorporated into these studies to gain knowledge of the mechanisms of release. In addition to isotope release concentrations valence state and nuclide solution species experiments need to be performed. Solid state

analysis should include detailed mineralogic studies to identify alteration products such as recrystallized minerals.

Studies in this area will first combine the waste form + canister + host rock + equilibrated groundwater using as much site specific detail coupled with the most realistic repository conditions as possible. The effects of engineered barriers and backfill will be assessed by adding to this system as they are developed.

These tests will proceed from laboratory scale (inches) to intermediate scale (feet) size to take advantage of gaining as much information as possible from tests that are easier to fabricate and relatively inexpensive (laboratory scale) and to provide enough sample solution, waste form and rock media for the solid state, solution and sorption-desorption studies and address the effects of scale-up (intermediate scale). Coordination and planning of these tests with WISAP Task 4 will be discussed in the next presentation. Exhibit 11 reiterates the objectives of the Phase II studies.

A proposed Phase III deals with full-scale testing of the Phase II integrated system. Although it is not a part of the WISAP program at this time, attention needs to be paid to these tests as a method to verify laboratory-scale results and serve as a final demonstration. Planning to date has been via WISAP Task 2 and Task 4 involvement with the ONWI In-Situ Demonstration Workshop, August 29-30, 1978, and more recently with the Earth Sciences Technical Plan.

In conclusion, the WISAP Task 2 is summarized as follows:

- Determine radionuclide release rates as a function of:
 - Leach solution of flow rate
 - Temperature
 - Leach solution composition
 - Time
 - Candidate repository waste forms
- Study waste form system performance (waste form + canister + engineered barrier + backfill + host rock)

- Provide a direct link to migration studies
- Study generic and site specific conditions
- Develop a release model based on mechanistic understanding
- Provide a leaching data bank

EXHIBIT 1. WISAP 2: Waste Form Release Rate Analysis

Objectives

- Determine release rates of radioisotopes from waste forms that may be used for geologic disposal of nuclear wastes
- Study release rates simulating near term, static, and long term leaching scenarios in generic and site specific geologic media
- Investigate the physicochemical phenomena governing waste form leaching under simulated repository conditions
- Provide data bank/release model for release consequence analysis
- Provide characterized waste form leachates for transport studies.

EXHIBIT 2. WISAP Task 2: Waste Form Release Rate Analysis

EXHIBIT 3. WISAP Task 2: Waste Form Release Rate Analysis

EXHIBIT 4. Non-Flow Release Studies - PNL

Objectives

- Study release for low temperatures and long times
- Gain understanding of effect of generic leachates
- Compare IAEA and static tests and study effects of buildup of chemical species in solution
- Use of static and IAEA tests on spent fuel and waste glass.

EXHIBIT 5. Continuous Flow Tests - LLL

Objectives

- Study the effect of solution flow and temperature on release using generic leachates
- Compare flow test to IAEA test
- Design flow tests for incorporation of rock media
- Use of waste glass.

EXHIBIT 6. Autoclave Release Studies - PNL

Objectives

- Study release under high temperature conditions (100-250°C) and generic leach solutions
- Develop systems for cold, doped, and hot cell operation to include hot cell flow capability autoclaves
- Carry out tests of increasing complexity to include waste form, container, backfill, and geology coupled experiments
- Use of spent fuel and waste glass.

EXHIBIT 7. Release Model Development - PNL, ANL

Objectives

- Analyze leachate solutions for speciation and particle size information
- Study the effect of anaerobic leachates on release
- Initiate oxidation and thermochemistry experiments on spent fuel
- Determine elemental profiles into leached surfaces and correlate data to leachate analyses from other subtasks
- Develop physical/chemical model of release behavior
- Spent fuel and waste glass.

EXHIBIT 8. Transuranic Waste Release Studies - BNL

Objectives

- Static, IAEA tests on TRU waste forms prepared from actual waste ash
- Selected actinide and fission product release as a function of temperature (25-75°C) and generic leachates
- Study concrete, polymer, urea-formaldehyde, and bitumen waste forms.

EXHIBIT 9. WISAP Task 2 Major Work Phases

Phase I	Parameter effects on waste form release
Phase II	Tests on waste containment systems
Phase III ^(a)	Full scale in situ or hot cell tests

(a) Suggested work to follow Phase II.

EXHIBIT 10. WISAP Task 2 Phase I Studies

- Determine the effect on waste form release from spent fuel, glass, and transuranic wastes as a function of:
 - a) temperature
 - b) leach solution chemistry
 - c) leach solution flow rate
- Obtain detailed elemental analysis of leachates
- Analyze waste form surface alteration and reaction products formed
- Define the leaching mechanisms
- Develop a model to describe waste form release

EXHIBIT 11. WISAP Task 2 Phase II Studies

- Study waste containment system performance under simulated repository conditions
- The waste containment system to be studied includes:
 - a) waste form
 - b) canister or container
 - c) buffer/backfill material
 - d) geologic media
- Tests will incorporate as much site specific detail as possible
- Refine and expand the waste form release model to include the full containment system.

4

1

WISAP TASK 4 (SORPTION-DESORPTION ANALYSIS)

by

R. J. Serne

The overall objective of Task 4 is to provide the WISAP Task 3, release consequence analysis modelers the necessary information on long-term migration potential of leached nuclear wastes. The data being generated on nuclide sorption-desorption and precipitation-dissolution is obtained by both theoretical and experimental studies. At present only rock-nuclide interactions in the far-field (away from the waste induced heat and radiation fields) are under the preview of WISAP Task 4. The transport rate of nuclides is quantified by measurement of a parameter called K_d , the distribution coefficient. There are several usages of the K_d parameter. A strict thermodynamic definition requires several conditions whereas an engineering or empirical usage of K_d requires few assumptions. The WISAP Task 4 usage is the latter. Thus K_d is defined as the ratio of the amount of nuclide adsorbed on the solid media (rock) divided by the amount of nuclide remaining in the contacting solution (groundwater). This distribution, for each nuclide, can be dependent on the rock type, groundwater composition, nuclide concentration, nuclide valence state, and rock-nuclide contact time and surface area contacted.

Presently the thrust of the Task 4 program is generic in nature. Until more direction and actual samples are available, work is being performed to gather data on nuclide-rock interactions for a wide range of rocks and groundwater types. To perform safety assessments the minimum nuclide-rock interaction data which should be supplied are the distribution coefficients (K_d 's) and nuclide solubility products (K_{sp} 's). The latter allow upper limits to be estimated for concentrations of nuclides in groundwater which can be used in simplified worst case calculations. As the safety assessment is most concerned with long-lived, biologically toxic nuclides, the following priorities have been established among all the possible fission products, actinides, and activation products. Highest priority for data collection is found for Tc, Pu, Np, I, U, Cs, Ra, and Sr. Other elements which are being more than just

curiously studied include C, Am, Sm, Ni, Se, Cm, Zr, and Sm. From past work, the adsorption of ^3H is being neglected and thus $K_d(^3\text{H})$ is assumed to be zero.

In the sizable experimental program under way numerous parameters are being monitored. These include rock-nuclide contact time, complete characterization of host rock and alteration products, complete characterization of groundwater, nuclide concentration, and valence stated distribution. As stated earlier, the present work is far-field and thus only temperatures between 20–80°C are considered.

In order to quantify the migration potential of nuclides, statistical techniques are being used to evaluate the functional dependency of the nuclide K_d or K_{sp} on the parameters being monitored, such as the influences of ion exchange, surface adsorption and mineral precipitation (all depicted in Exhibit 9). The experimental data and statistical predictor equations by themselves will not provide identification of adsorption mechanisms but they will provide empirical data in a timely fashion to assess migration from repositories. Other more systematic and detailed studies (not discussed herein) are under way to start identifying mechanisms in hopes of generating truly generic predictor capabilities based on adsorption/precipitation mechanism models.

Future plans include comparison of the described laboratory results with theoretical concepts, field observations and performance of verification or "validation" experiments. As the completed laboratory experiments can be typified as being short-term in time and pathlength when compared to possible repository breaches, studies to extrapolate to tens or hundreds of thousands of years and kilometers must be undertaken. Long time frames can be addressed using thermodynamic constructs such as weathering, ore deposition, mineral stability and Eh-pH diagrams. Field observations such as the Oklo natural reactor and ore deposits (especially uranium) allow observations over the time frame of interest. Other man-made "disposal sites" at Nevada Test Site, DOE and shallow land burial sites allow extrapolation to tens of years and long pathlengths. Future repository site verification will include experiments

(tracer well tests, in-situ migration tests, etc.). Also, as possible sites are identified, adsorption work will shift to site-specific experiments on actual core material.

Finally, an area which will be addressed is the merging of Task 2 Waste Form Release Rate Analysis (by definition near-field), and Task 4 Sorption-Desorption Analysis to address near-field waste-rock-water-nuclide interactions. Exhibit 13 portrays the near-field regime with some of the proposed materials and potential interactions. Presently Task 2's experimental program is typified as working on the binary system waste form plus solution. The waste forms under current study include spent fuel, "cold and doped waste glass and various solidified forms of transuranic wastes. In the case of the simple waste form, solution system, nuclide release is commonly described by a leach rate. One must understand this system (in the event of failure of the other barriers) and also the total system of waste form, groundwater, canister, engineered barrier, backfill, and host rock interactions. In the latter case, release is a combination of leaching and sorption/desorption interactions complicated by re-crystallization and precipitation reactions. One is forced to talk about a "system release" rate in this latter case.

It must be pointed out that sorption/desorption analysis is an intimate part of these systems studies. The combination of waste form leaching, the mineralogic alteration of the waste package system, and sorption reactions control the nuclide source term from the very near-field. This source term is used for the far-field nuclide sorption studies, thus making the connection from the waste form to far-field migration.

Additional experiments planned on the total system are shown on Exhibit 15. The progression from simpler experiments to the actual large-scale verification experiments is outlined on Exhibit 16.

EXHIBIT 1. Waste Isolation Safety Assessment Program
(WISAP)

Task 4

Sorption-Desorption Analysis

Task Leader
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EXHIBIT 2. Objective

To obtain from theoretical and experimental studies quantitative data to describe the long-term, far-field radionuclide-geologic media interactions which affect the transport of nuclear wastes.

By the end of FY-1981 sufficient data should be available to evaluate the long-term fate of nuclides leached by groundwater from solid waste forms.

EXHIBIT 3. Far-Field Studies

- Outside region of waste induced temperature and radiation effects
- Normal rock-water weathering and rock-leached nuclide interactions

EXHIBIT 4.

$$K_D = \frac{\text{Amount of nuclide sorbed on solid}}{\text{Amount of nuclide remaining in solution}}$$

EXHIBIT 5. Existing Experimental Program

Generic studies on a wide range of rocks and groundwater types

EXHIBIT 6. Minimum Data Needed

- Nuclide distribution coefficients (Kd's)
- Nuclide solubility products (Ksp)

EXHIBIT 7. Elements with Biologically Hazardous Radioisotopes

First concern

Tc, Pu, Np, I, U, Cs, Ra, Sr

Secondary concern

C, Am, Sn, Ni, Se, Cm, Zr, Sm

EXHIBIT 8. Parameters Monitored

- Time
- Complete characterization of host rock and alteration products
- Complete characterization of groundwater
- Nuclide concentration
- Nuclide valence state
- Temperature (~20–80°C)

EXHIBIT 9

EXHIBIT 10. Raw Output

Kd or nuclide solution concentration as a function of

- a) Host rock mineralogy, exchange capacity and surface area
- b) Groundwater composition, pH and Eh
- c) Nuclide Concentration
- d) Nuclide valence state
- e) Time

EXHIBIT 11. Refined Output

- Kd data bank
- Multinomial Kd predictor equations
- Adsorption precipitation mechanism models
- Understanding of trace constituent migration in geohydrologic system

EXHIBIT 12.

- Validation
- Theoretical concepts
 - a) weathering
 - b) ore deposition geochemistry
 - c) mineral stability
 - d) thermodynamic Eh-pH diagrams
- Field observations
 - a) Oklo natural reactor
 - b) Nevada test site
 - c) grants mineral belt uranium deposit
 - d) shallow land burial sites
- Validation experiments
 - a) field studies
 - b) in-situ tests
 - c) intact core (laboratory)

EXHIBIT 13. Near Field Interactions

EXHIBIT 14. Existing Experimental Program

- Simple system = waste-water leach tests
- Waste forms
 - a) spent fuel
 - b) doped glass - high level glass
 - c) transuranic wastes

EXHIBIT 15. Additional Experiments Planned

- Total system = waste form, canister, backfill, engineered barrier, host rock, and groundwater
- Will study all in concert and as ternary systems
 - a) Effects of
 - 1. canister corrosion products
 - 2. backfill/engineered barrier products
 - 3. groundwater compositionon waste form leaching
 - b) Effects of backfill, engineered barriers, and host rock reactions on nuclide release
 - 1. remineralization
 - 2. precipitation
 - 3. sorption
 - c) Look for synergistic/antagonistic reactions

EXHIBIT 16. Planned Experimental Design

- Scaled waste forms in canister placed in host rock core with backfill and barriers. Whole system placed in flow through autoclave. Eventually in-situ field verification
- Will use "cold" waste, "doped" waste, and actual waste
- Actual waste in remote controlled hot cells

NON-FLOW RELEASE STUDIES

by

D. Bradley

The subtask with this title encompasses all the tests at PNL that are not run above 100°C, which falls into the Autoclave release subtask. Currently we are conducting IAEA and static leach tests in parallel on both spent fuel and cold and actinide doped waste glasses.

The IAEA tests on actinide doped glass have been going for the longest time (roughly 1.5 years) whereas the static tests have only recently started. Because of a shortage in analytical help at the time when the tests were generating the most samples, we are still catching up on a considerable sample backlog. Work is proceeding quite well in this area but to date only the IAEA test on actinide doped glass has had enough leach solutions analyzed for presentation at this time.

Exhibit 1 shows some characteristics of the IAEA test, and Exhibit 2 details the IAEA sampling schedule that we used. Exhibit 3 depicts the IAEA leach test container apparatus.

In order to study isotopes of long-term potential hazard without the high radiation fields of actual high-level waste, sample waste forms were made using these isotopes alone. Four glasses, based on the same composition, were made incorporating the following isotopes:

1. ^{99}Tc
2. ^{244}Cm
3. $^{233}\text{U} + ^{243}\text{Am}$
4. $^{237}\text{Np} + ^{239}\text{Pu}$

These isotopes were doped into the waste glass to the extent normally present in high level waste. The assumptions for this reference waste were:

1. burnup = 33,000 MWD/MTU
2. reactor type = reference PWR, 3.3% enriched
3. age of waste = 2 yr old
4. reprocessing loss = 0.5% U + Pu
5. specific power = 26.4 MW
6. waste loading = 33% (fission products + actinides + reprocessing chemicals).

The doped glasses, except for the ^{233}U series, contained the expected amount of uranium as ^{238}U .

As a compromise between the reality of cracked glass monoliths and the powdered glass frequently studied in accelerated leach testing, glass beads were chosen as the sample waste form for study. A resistance heated unit was installed in a glove box for preparation of the doped glasses. The process involves heating a comparatively large volume of glass to the melt temperature, continuously forming droplets at the end of a nozzle, and collecting the solid beads on a heated metal plate.

The procedure for making doped glass beads using the resistance heated unit has the following steps:

1. Frit and calcine (33% calcine for NFS glass) are placed in a platinum crucible and melted (1050°C for NFS glass), the melt is cooled to form undoped solid glass.
2. The weighed dopant is dissolved in 6N HNO_3 . This is done with a minimum of liquid and heating. HNO_3 with 5% HF is used to dissolve NpO_2 and PuO_2 . A clear solution is obtained. Aliquots of the solutions are retained for future analysis.
3. The preformed NFS glass is crushed to -40+60 mesh, weighed, and thoroughly "wetted" with the dopant solution.
4. The wetted glass is vacuum dried and preheated to 500°C to reduce nitrate concentration (causes glass frothing).

5. The glass is melted in stainless steel crucibles for 2 hr at 1050°C, water quenched, and broken out of the crucible.
6. The glass is placed in a quartz bead making tube, the temperature adjusted to 1050-1100°C, and the beads collected on steel pans maintained at 400°C.
7. The beads are annealed for 2 hr at 500°C and cooled to ambient temperature at 100°C/hr.

The resulting glass composition is shown in Exhibit 4, along with frit and calcine compositions. Exhibit 4 is specific for the glass doped with ^{237}Np and ^{239}Pu . The concentration of the dopants (corrected for volatilization losses in the case of ^{99}Tc) are:

$$\begin{aligned}
 ^{99}\text{Tc} &= 4.6 \times 10^{-3} \text{ g/g glass} \\
 ^{233}\text{U} &= 3.7 \times 10^{-2} \text{ g/g glass} \\
 ^{237}\text{Np} &= 4.1 \times 10^{-3} \text{ g/g glass} \\
 ^{239}\text{Pu} &= 4.1 \times 10^{-4} \text{ g/g glass} \\
 ^{243}\text{Am} &= 1.1 \times 10^{-3} \text{ g/g glass} \\
 ^{244}\text{Cm} &= 1.2 \times 10^{-4} \text{ g/g glass}
 \end{aligned}$$

Approximately 1.5 kg of doped glass beads were prepared in four separate runs with the resistance unit. Exhibit 5 summarizes the bead characteristics. The confidence limits shown are at one standard deviation. Thus, the beads had constant properties to within a few percent. This illustrates that a major value of this approach is reproducibility of sample preparation.

Random samples of the beads were examined by X-ray diffraction, metallography, and α -radiography. X-ray diffraction traces of the various glass preparations are shown in Exhibit 6. Weak reflections from a spinel type oxide (MO_2 ; $\text{M} = \text{U}, \text{Ce}$) are observed in the 1-3 wt% range. The actual concentration varies somewhat from sample to sample because these "difficult to solve" phases tend to form clusters. Small concentrations of Pd metal and RuO_2 are also present in the glass but

≤ 1 wt%. All of these phases are common to waste glass compositions. At this relatively low concentration level and small crystal size (mainly $\leq 1\mu\text{m}$) they do not appear to adversely affect any of the properties of the glass, at least with regard to dispersibility

Optical micrographs and autoradiographs are shown for three of the doped glasses in Exhibits 7-9.

The porosity of all of the beads, except for the ^{99}Tc beads, was less than 3%, which is lower than that measured in a full-scale canister of glass produced by the in-can melting (ICM) process.⁽¹⁾ In any case, the porosity will not affect the leaching studies now under way. Even after 2 yr at a leach rate of $1 \times 10^{-5} \text{ g/cm}^2\text{-day}$, the depth of glass penetrated would only be $\sim 20\mu\text{m}$. However, after high temperature autoclave work is completed, corrections for the internal area may be necessary if extensive dissolution of the glass occurs.

The autoradiographs for $^{237}\text{Np} + ^{239}\text{Pu}$ and ^{244}Cm doped glasses show that these isotopes are very evenly distributed through the glass. For the case of the ^{99}Tc doped glass, the porosity of the bead has an immediate effect on the leach resistance. It appears that Tc has concentrated in the small voids in the glass, having lower concentration in the bulk. Thus, the initial leach rates are high as Tc is leached from the void on the surface. Further studies are being planned to investigate the behavior of Tc in glass made by full-scale equipment using Tc doped waste calcine. Therefore, the leaching data presented should be regarded as preliminary.

Large spinel phase inclusions which form by corrosion of the steel melting crucible (and also occur in full-scale ICM glasses) are seen to be highly depleted in actinides, as expected. The porosity in the glass tends to give a false impression of irregular α -tracking and some dark spots seen are anomalies of the film processing and radiography technique.

Twenty beads (~ 1/3 gram each) were used per leach test. The ratio of solution volume to sample surface area was 10/1. This marks out to be 300 ml of solution per test. The five leach solutions that were used are described in Exhibit 10.

Prior to beginning the leaching procedure, the beads were washed in ethyl alcohol, weighed, and put in vials of 20 each. Each leach experiment used 20 beads suspended in a nylon basket centered in 300 ml of solution. The leach containers were polypropylene-jars with O-rings fitted into the lids to assure a good seal.

On a given sample day, the basket holding the beads was carefully removed and a sample withdrawn after swirling the jar of solution. This sample was then acidified to a pH of 1 using concentrated nitric acid. This sample was then analyzed for the particular isotope(s) the glass was doped with. To check that this is effective in preventing isotopes from adhering to the sample container walls, another acid strip plus counting the sample container was done after the original solution was used. The pH 1 solution proved to be quite effective as insignificant amounts were found on the container walls. The original polypropylene jar was now filled with 300 mls of 5 M HNO_3 + 0.05 M HF. This solution was used to remove any isotopes that had adhered to the jar walls. After a period of time, equal to the original leaching period, a sample was withdrawn and analyzed. The results of both of those analyses were added to give the total amount leached from the glass during the leach period.

The major finding on actinide plate out is that during the early leaching period, the plate out contribution is small but after 20-40 days can become equal to the contribution found in the leach solution. A more detailed analysis of the actinide plate out on the leach test container walls will be given in a document to be published in October 1979.

The equation used to calculate the isotopic leach rates and cumulative fractions leached are as follows:

$$R_i = \frac{a_o}{A_o S t} ; \quad \Sigma R = \frac{\Sigma a_o}{A_o W}$$

Where R_i = Incremental leach rate in $\text{g/cm}^2\text{-day}$
 a_o = Activity of isotope in leachate, sec^{-1}
 A_o = Specific activity of isotope in sample,
 $\text{sec}^{-1} - \text{gram}^{-1}$
 S = Geometric surface area of sample, cm^2
 t = Leaching time, days
 ΣR = Cumulative fraction leached
 W = Sample weight, grams

Exhibits 11 and 12 show the leach rate curves for ^{239}Pu as a function of time and solution composition. The trends seen here are also followed by ^{237}Np and ^{244}Cm . As can be seen from these figures, the leach rate drops by a factor of 10 in the first 10 days for all solutions. The leach rates tend to level off after this time. There is also an order of magnitude difference in leach-rates between WIPP "B" brine and bicarbonate solution with bicarbonate solution having the higher leach rate. Curium follows plutonium closely in these trends, neptunium shows less of a spread between solutions. The bicarbonate was expected to show a higher release rate because the high pH (~ 8.5) tends to accelerate the dissolution of the glass matrix.⁽²⁾ The leach behavior in deionized water for ^{239}Pu and ^{244}Cm is following very closely with that observed in a previous test using a fully radioactive waste glass and the same test procedure.⁽³⁾ Data on ^{233}U and ^{243}Am will be reported this fall as it is not presently available.

Exhibit 13 shows the leach rates of ^{99}Tc in WIPP "B" brine and deionized water only, as the other solutions fell between them. The trends seen here are quite different from those just discussed. The leach rates are quite high at first but then fall steadily. After 400 days the leach rate has fallen by more than a factor of 10,000. This trend is probably attributed to

the fact that Tc seems to accumulate in small voids present in the glass (see Exhibit 9) leaving a lower concentration in the bulk matrix. Once the surface voids are leached, the lower concentration in matrix causes a lower calculated leach rate since they are based on a homogeneous distribution in the glass. As mentioned previously, further studies are needed to learn how Tc goes into high level waste glass. We will also try to learn what fraction of the Tc has concentrated in the voids.

Exhibits 14-17 show cumulative fraction curves for ^{237}Np , ^{239}Pu , ^{244}Cm , and ^{99}Tc . The differences between solutions and isotopes are more apparent here. Again we see a factor of 10 spread between solutions with bicarbonate having the highest release. Neptunium at this point appears to be leaching 5 to 10 times faster than Pu which in turn is of that magnitude faster than Curium.

The accelerated leaching behavior of Curium in deionized water is unexplained at this time.

Figure 17 shows the cumulative fraction leached for ^{99}Tc . It is nearly flat as expected in view of the large drop in leach rate with time. It is interesting to note that after nearly 500 days of leaching, its fraction leached is practically the same as Cesium and Strontium from a fully radioactive glass sample leached for nearly the same time.⁽³⁾

At the present time we are analyzing solutions from the $^{233}\text{U} + ^{243}\text{Am}$ leach test along with more samples from the ^{244}Cm and $^{237}\text{Np} + ^{239}\text{Pu}$ leach tests. Metallography is being performed on one complete series of these IAEA tests (which were run in triplicate) that have been leaching for nearly 500 days. This will yield information on the surface alteration of the glass. We will also have a complete series of solutions analyzed by induction coupled plasma (ICP) spectroscopy to obtain leach rates for a wide variety of elements including glass matrix components.

REFERENCES

1. Larsen, D. E., and W. F. Bonner, editors. 1976. High Level Waste
Vitrification by Spray Calcination/In-Can Melting. BNWL-2092, Pacific
Northwest Laboratory, Richland, WA.
2. Hench, L.L. January 4-5, 1977. "Leaching of Glass." Presented at a
Workshop held at ERDA - Germantown on Ceramic and Glass Radioactive Waste
Forms. CONF-770102.
3. Bradley, D. J. September 1978. Leaching of Fully Radioactive High-Level
Waste Glass. PNL-2664, Pacific Northwest Laboratory, Richland, WA.

EXHIBIT 1. IAEA Leach Tests

- Change complete leach solution according to prescribed schedule
- Ambient temperature
- Models dynamic flow situation
- An international standard test
- Models contact with waste form after decay to low heat generation, long-term boundary condition

EXHIBIT 2. IAEA Leach Schedule

<u>Cumulative Time</u>	<u>Leach Solution Changed</u>	<u>Series Number</u>	<u>Leach Solutions Analyzed</u>
Days	1	1	1
	2	2	2
	3	3	3
	4	4	4
Weeks	2	5	5
	3	6	6
	4	7	7
	5	8	8
	6	9	
	7	10	9
	8	11	
	9	12	10
Months	3	13	11
	4	14	
	5	15	12
	6	16	
	7	17	13
	8	18	
	9	19	14
	10	20	
	11	21	15
	12	22	

EXHIBIT 3. IAEA Leach Test Container

**EXHIBIT 4. Composition of Frit, Wastes, and Doped Waste Glass
Used for Actinide Release Studies**

Frit Composition, ^(a)		Waste Calcine Composition, ^(b)		Glass Composition, ^(c)	
wt%		wt%		wt%	
59.7	SiO ₂	29.2	Fe ₂ O ₃	40.0	SiO ₂
14.2	B ₂ O ₃	15.0	Na ₂ O	12.5	Na ₂ O
11.2	Na ₂ O	12.6	²³⁸ U ₃ O ₈	9.6	Fe ₂ O ₃
7.45	ZnO	6.8	MoO ₃ ^(d)	9.5	B ₂ O ₃
4.45	TiO ₂	5.3	ZrO ₂	5.0	ZnO
3.0	CaO	5.0	Nd ₂ O ₃ ^(e)	4.2	²³⁸ UO ₂
		3.6	CeO ₂	3.0	TiO ₂
		3.2	RuO ₂	2.2	MoO ₃
		3.1	Cs ₂ O	2.0	CaO
		1.7	BaO	1.7	ZrO ₂
		1.6	PdO	1.65	Nd ₂ O ₃
		1.6	La ₂ O ₃	1.19	CeO ₂
		1.6	Pr ₆ O ₁₁	1.07	RuO ₂
		1.41	²³⁷ NpO ₂	1.03	Cs ₂ O
		1.4	P ₂ O ₅	0.56	BaO
		1.2	Cr ₂ O ₃	0.53	PdO
		1.1	SrO	0.53	La ₂ O ₃
		0.98	Sm ₂ O ₃	0.53	Pr ₆ O ₁₁
		0.78	TeO ₂	0.46	²³⁷ NpO ₂
		0.64	Y ₂ O ₃	0.46	P ₂ O ₅
		0.60	NiO	0.40	Cr ₂ O ₃
		0.52	Rh ₂ O ₃	0.37	SrO
		0.38	Rb ₂ O	0.32	Sm ₂ O ₃
		0.21	Eu ₂ O ₃	0.26	TeO ₂
		0.15	Gd ₂ O ₃	0.21	Y ₂ O ₃
		0.140	²³⁹ PuO ₂	0.20	NiO
		0.10	CdO	0.17	Rh ₂ O ₃
		0.090	Ag ₂ O	0.13	Rb ₂ O
				0.070	Eu ₂ O ₃
				0.050	Gd ₂ O ₃
				0.046	²³⁹ PuO ₂
				0.033	CdO
				0.031	Ag ₂ O

- (a) 76-101 Frit.
 (b) PW-8a-3 Calcine. } PNL Waste
 (c) 76-68 Glass. } Form Identifiers
 (d) Chemical Stand-In for Mo + TC.
 (e) Chemical Stand-In for Nd, Am, and Cm.

EXHIBIT 5. Doped Glass Bead Characteristics

	Dopants			
	<u>^{244}Cm</u>	<u>^{99}Tc</u>	<u>$^{237}\text{Np}/^{239}\text{Pu}$</u>	<u>$^{233}\text{U}/^{243}\text{Am}$</u>
Beads Produced	400	450	2400	650
Mass (g/bead)	0.459 ± 0.024	0.362 ± 0.006	0.353 ± 0.013	0.381 ± 0.005
Density (g/cm ³)	3.040 ± 0.004	3.042 ± 0.025	3.028 ± 0.038	2.974 ± 0.015
Diameter (cm)	0.759 ± 0.010	0.683 ± 0.008	0.681 ± 0.008	0.696 ± 0.005
Eccentricity (%)	0.7	0.3	0.5	0.3
Height (cm)	0.455 ± 0.005	0.437 ± 0.008	0.437 ± 0.005	0.442 ± 0.003
Amount of Isotope g/g glass	2.44×10^{-4}	Being Analyzed	$^{237}\text{Np } 4.08 \times 10^{-3}$ $^{239}\text{Pu } 4.13 \times 10^{-4}$	$^{243}\text{Am } 8.62 \times 10^{-4}$ $^{233}\text{U } 2.46 \times 10^{-2}$

Average "second" phase concentrations - for all beads.

1-3% M_3O_4 - spinel, M + Fe, Cr, Ni, Zn

1% MO_2 - fluorite, M = U, Ce

0-3% porosity

EXHIBIT 6. X-ray Diffraction Patterns for Doped Glasses

EXHIBIT 7.

Pu, Np

OPTICAL

1 mm

RADIOGRAPH

EXHIBIT 8.

Cm

OPTICAL

1 mm

RADIOGRAPH

EXHIBIT 9.

Tc

OPTICAL

1 mm

RADIOGRAPH

EXHIBIT 10. Waste Form Leach Solutions

- Salt brine, WIPP "B" natural salt brine
- Synthetic high ionic strength groundwater (30 meq/l CaCl_2)
- Synthetic high bi-carbonate groundwater (30 meq/l NaHCO_3)
- Synthetic high ionic strength groundwater (30 meq/l NaCl)
- Deionized water

EXHIBIT 11. IAEA Leach Test

EXHIBIT 12. IAEA Leach Test

EXHIBIT 13. IAEA Leach Test

EXHIBIT 14. IAEA Leach Test

EXHIBIT 15. IAEA Leach Test

EXHIBIT 16. IAEA Leach Test

EXHIBIT 17. IAEA Leach Test

AUTOCLAVE RELEASE STUDIES

by

J. H. Westsik, Jr.

The objective of this subtask is to examine the behavior of a high-level waste glass and spent fuel in aqueous solutions at high temperatures and pressures. By studying the waste water interactions we will 1) generate leach rate data, 2) gain some understanding of the kinetics and mechanisms of the interactions, 3) simulate long time, low temperature leaching, and 4) provide input to the leach model subtask.

To meet these objectives, the experiments are designed to start with tests on simple systems and then to progress to more complicated ones. Thus, the initial tests are examining the interaction of just the waste and the solution. Later work will include additional factors, and finally the waste, canister, backfill, geology, and solution system will be studied. Both static and flowing configurations will be used.

The waste glass will be studied in three forms—undoped, doped with actinides, and fully radioactive prepared from actual high-level wastes. The undoped and doped glasses are used because of ease of handling and availability of analytical instrumentation for surface analysis. The fully radioactive glass is used to verify the results of the other glass forms and to study nuclides not simulated in the doped glasses.

The current autoclave studies are evaluating the waste-water interaction as a function of temperature, time, and solution composition. Small, 1/3 g glass beads are sealed in gold capsules containing deionized water, a 2.52 g/l sodium bicarbonate solution, or the WIPP B brine. The solution volume to glass surface area ratio is 10 cm. The samples are held at 150°C or 250°C and 2000 psi for times of 2, 4, 8, 16, or 32 days. Other static tests are being run at 25° and 75°C so that some kinetic information will be obtained over a broad temperature range. Replication is achieved by running separate tests

with undoped beads and with beads doped with ^{99}Tc , ^{244}Cm , ^{233}U + ^{243}Am , or ^{239}Pu + ^{237}Np . After the test, the solutions are analyzed for the glass components and the glass beads are examined for reaction layers and alteration products.

Visual examination of the undoped beads revealed no changes after 150°C treatments in any of the three solutions. After exposure to 250°C WIPP B brine, the beads showed some pitting of the surface. No reactions appeared on the bicarbonate beads. The beads reacted with deionized water at 250°C developed an orange milky surface coloration. X-ray fluorescence analysis of the surface showed some gold but not enough to account for the color change. Additional surface characterization is needed.

Exhibits 1 and 2 show weight loss data as a function of time for the 150° and 250°C tests. As expected, the weight losses are higher at the higher temperature. The rate of weight loss, as indicated by the slopes of the curves, decreases with time. This suggests that saturation effects may be limiting the rate of attack of the glass. There is no difference in the weight loss rates to deionized water and the bicarbonate solution. Weight losses in the salt brine are about 2-1/2 times lower at 150° and 4 times lower at 250°C than in the lower ionic strength solutions.

Weight loss measurements do not tell, however, how the individual glass components are behaving. Exhibits 3 and 4 show cesium concentrations in solution as a function of time. These concentrations were measured at 25°C and therefore may not include material that precipitated as the solutions were cooled from 150° and 250°C. As seen with the weight loss measurements, cesium releases are higher at the higher temperature and the rate of release is decreasing with time. Solution effects are different though. At 250°C more cesium is found in the brine than in the other solutions. At 150°C, cesium is again released most to the brine, but more cesium is released to the sodium bicarbonate solution than to deionized water. This relative order of release probably results from the relative sodium and hydrogen ion concentrations in the three solutions. The brine has the highest concentration of ions free to exchange with the cesium in the glass, deionized water has the least.

Analysis of data from the current autoclave tests shows that temperature, time, and solution composition all influence the behavior of waste glass in hydrothermal environments. These tests will continue with additional solution analysis for other glass components and with examination of the glass surfaces. Tests needed to investigate the effects of solubility and saturation on the glass behavior will be started this fall at PNL. The information from these tests will complement those just described. The tests will then expand to include more complex systems involving fully radioactive glass and spent fuel. A document describing the first series of waste-glass solution interactions is expected to be finished by late fall 1979.

EXHIBIT 1. Weight Loss at 150°C

EXHIBIT 2. Weight Loss at 250°C

EXHIBIT 3. Cesium Releases at 150°C

EXHIBIT 4. Cesium Releases at 250°C

EXHIBIT 3. Cesium Releases at 150°C

EXHIBIT 4. Cesium Releases at 250°C

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RELEASE MODEL DEVELOPMENT

by

R. P. Turcotte

Although leaching studies of nuclear waste glasses and other solid forms have been part of every development effort, we are not yet at a point where a defensible "leach model" can be presented. A major result of our work during the last year has been a clearer recognition that leaching models proposed previously, based on studies of simple glasses, are simply not applicable to typical nuclear waste glasses. Models based on combinations of diffusion and corrosion mechanisms which give apparently good agreement with experimental data (for a single element) in fact give very poor agreement if data for all of the elements present are considered. The main finding is that "corrosion," as meaning that all elements are congruently removed, has not yet been shown to occur. The recent studies of hydrothermal reactions of waste glasses give clear examples of how unimportant both diffusion and corrosion can really be. Exhibit 1 shows a typical result of a severe hydrothermal test of waste glass 76-68. The pellet has been hydrothermally reacted through its entire volume, causing about 50% crystallization and formation of some major cracks. At high magnification, the microstructure, as shown, consists of a relatively uniform dispersion of very fine crystals ($<1\text{ }\mu\text{m}$) in an amorphous, clay-like matrix. While alteration of this kind is not desirable, little material is actually leached away as shown by microprobe analysis of the solid and by solution analyses. As shown in the exhibit, the solution concentrations of Cs and Sr are in the ppm range in deionized water and reach hundreds of ppm in salt brine experiments.

The point here is that solubility constraints play an important role—high temperatures can cause alteration of glasses and crystalline waste forms (to a lesser extent) but material entering the aquifer is restricted. Exhibits 2 and 3 give additional examples of leaching behavior (at 25°C) also directly affected by solubility limitations. In Exhibit 2, results are compared for a stagnant leach test, versus a test in which deionized water is

periodically replaced. After a few months, the apparent leach depth (based on Cs analysis) for the stagnant case begins to flatten. With fresh water additions, the penetration depth continues to increase. In Exhibit 3, the apparent leach rate of a solid cylinder is two orders of magnitude larger than for the same glass in crushed form. In the case of the powdered glass the solution concentrations are much higher than in the solid cylinder test--the system rapidly approaches the "solubility limit" for Cs, hence the apparent leach rate is dramatically lower.

Exhibits 4 and 5 summarize in a schematic manner the two limiting cases we need to recognize in all of our leaching studies. Although the example shown is for glass, the concept applies to all waste forms. In a closed system (Exhibit 4), or in slow groundwater flow conditions, chemical back-reactions and elemental solubility limits become the rate controlling considerations. We know that alkali elements like Cs will achieve much higher solution concentrations than will the insoluble actinide elements, like Pu. With glasses, the formation of a gel layer can actually result in decreasing solution concentrations as shown by the work reported later by G. McVay (this meeting). In Exhibit 5, showing the open system (high groundwater flow) case, it can be possible that saturation limits are not approached and the fractional losses continue with time, depending on ion mobilities in the gel, removal of structural silica, elemental bond strengths, etc.

The scientific description of these leaching processes is obviously a great challenge but will be the foundation of important "hazard to man" analyses undertaken within the framework of the WISAP effort. The leach model we are attempting to develop is, therefore, more than a simple technical description of specific leach tests. Exhibit 6 outlines where we hope to be going in terms of "Model Development." Right now, all of the work within Task 2 is involved in parametric tests of the major factors controlling leach rates. Later this year, coupled experiments, including the waste forms, canister, rocks and equilibrated groundwater will simulate actual repositories. Large scale "Validation" tests will eventually be required.

The composite of experiments in all of these areas will form the "Leach Model." Exhibit 7 gives an idea of some of the considerations needed in actually trying to take simple laboratory experiments and then applying them to a hypothetical repository. The outline shown is not complete but gives some idea of the complexity of the problem even in its most simple form.

Finally, it is important to recognize that results of other studies on waste glasses and alternate waste forms are being factored into the WISAP program. We are aware that different glass compositions behave somewhat differently, that crystalline materials will be different than glass, that radiation damage effects need to be considered, etc. Most of these questions are being addressed outside of the immediate objectives of WISAP Task 2, especially on the HLWIP program at PNL. A great deal of complementary information on glass (76-68), in particular, greatly strengthens the work on WISAP. Studies of crystalline waste forms, including supercalcine and Synroc, are in progress, using the same procedures followed in WISAP. As an example of the glass work undertaken, Exhibit 8 shows some leach data plotted as a function of compositions for an 11 component system. A similar study of glasses covering the entire range of compositions being considered in the U.S. will begin later this year, using the same static tests defined by WISAP studies.

With respect to a leach model for crystalline materials, we already know that glasses, spent fuel, supercalcine, etc., give comparable leach rates in simple tests. While a technical description of the leach process in these materials must be quite specific to the waste form, and surrounding environment, part of our continuing effort will be to incorporate the common features, such as the role of elemental solubility limits, into empirical models. Since the work on these materials is very limited, any modeling work is premature. The work in the spent fuel area is covered by B. Katayama (this meeting).

EXHIBIT 1. Glass 76-86

Hydrothermal Leach Test, 350°C - 3 Weeks, Deionized Water
Saturation Concentrations After 350°C Tests

	<u>Deionized H₂, ppm</u>	<u>Salt Brine, ppm</u>
Cs	37	500
Rb	24	64
Sr	1.3	160
Ba	—	—
Mo	940	45

EXHIBIT 2. A Comparison of Stagnant Versus Dynamic Leach Test Results

EXHIBIT 3. Leach Rates Based on Cs from Solid and Powdered Samples of 76-68 Glass

EXHIBIT 4. Glass, Closed System (Low Flow)

EXHIBIT 5. Glass, Open System (High Flow)

EXHIBIT 6. Leach Model Development

EXHIBIT 7. WISAP Source Term

I. Repository conditions

1. T history, nuclide decay subroutine
2. water quality, flow rate
3. dimensional drawing(s) of near field to include
 - canister size
 - free volume around canister
 - fracture/flow pattern in bedrock

II. Canister failure kinetics

1. "Simple" corrosion
2. Stress cracking, pitting
3. Estimates of size of breach

III. Leaching of exposed glass

1. Area exposed = canister crack area
2. Monolith exposed = geometric area
3. Leach surface area = crack surfaces (total)
4. Radial dependence on surface area
5. $T/(SA/V)/\text{flow rate}/\text{solution composition}$
6. Evaluation of above (esp. 3) relative to ion diffusion in solution phase, solubility limit, etc.
7. Effects of surrounding media.

IV. Transport of leached material--away from canister and interface

Task 4 (sorption)

1. Transport without sorption
 - water flow limited
 - ion diffusion effects
2. Transport with sorption

EXHIBIT 8. Effects of Components on Soxhlet Leach Rate

GAMMA-IRRADIATION EFFECTS ON LEACHING CHARACTERISTICS
OF WASTE CONTAINMENT MATERIALS

by

G. L. McVay

Materials which contain typical radioactive waste are subjected to gamma-irradiation from the waste itself. Therefore, it is important to understand the effect of this irradiation on the leaching characteristics of waste containing materials in the event of an exposure to water during the time span when significant gamma-irradiation is occurring. With this goal in mind, an experiment has been initiated to characterize the leaching behavior of 7668 glass, supercalcine ceramic, and UO_2 during exposure to gamma-irradiation.

This experiment consists of leaching and elemental analyses on samples both in and out of a gamma-irradiation field so that the effect of irradiation can be evaluated. Additionally, the dose rate effect on leaching is being investigated. At present, only the results from the 7668 glass and to a lesser degree from the supercalcine ceramic are complete enough to be reported.

Time dependent leaching results, without exposure to gamma-irradiation, have been obtained at 89°C for 7668 glass in distilled water for both the solid and the powdered states. The solid samples were leached at a sample surface area to leach solution volume ratio (SA/V) of 0.10. The accumulation of some of the key elements with time in the leach solution is shown in Exhibit 1, along with the time dependence of the leach solution pH. The leach solution undergoes a rapid change in pH initially, then changes less with additional time increments. Although it is difficult to see in this exhibit, most elements also show an initial large release rate into the leach solution which then decreases with time. A more informative way of presenting the same leach data is to normalize by the amount of elements originally in the glass and by the surface area exposed to the leach solution. The net result is the fraction of an element removed from the glass by leaching per unit surface area. The leach data originally shown in Exhibit 1 is presented

in this form in Exhibit 2. It can be seen from Exhibit 2 that two types of behavior are occurring. One group of elements (Na, Mo, B, and Si) are increasing in an essentially linear fashion with time while the other group (Cs, Sr, Ca, and Ba) are decreasing in concentration with time. Acid stripping of the leach container walls did not yield the elements in sufficient enough quantities to account for their decrease in the leach solution. Therefore, the elements are probably sorbing back onto the gel layer which is developing on the glass surface. This hypothesis is being tested with sample surface analyses. Additionally, the pH of the leach solution has gone above 8.5 which according to Hench's model should result in congruent dissolution. As can be seen from Exhibit 2, congruent dissolution is not occurring nor is any tendency in that direction observable. Thus, the model of Hench for glass corrosion is not applicable to 7668 glass.

Quite a lot of leach data has been reported on powdered samples. It is always a question whether this data can be used to predict what will happen to solid samples. Thus, for comparative purposes some minus 200 mesh 7668 glass powder was leached at 89°C in distilled water for various times and the results are presented in Exhibit 3. Surface area analyses, by BET, of the powder yielded 0.36 m²/g. The ordinate (fraction removal/cm²) is three orders of magnitude less than that for the solid samples. This has also been observed by others. These leach tests were static (no flow or agitation) and therefore the solution could become quite concentrated in ions around the glass particles which could slow down or stop leaching on a local scale. Furthermore, the pH rapidly becomes quite high and remained relatively constant thereafter. Since the pH was higher for the powder samples than for the solid samples, it is possible that different leaching behavior or mechanisms are occurring. Comparison of solid and powder leaching results (Exhibits 2 and 3) show similar trends for Cs, Ba, Ca, and Sr with the powder samples just compressing the time scale. However, Si behaves much differently. There appears to be a tendency for saturation of the elements in solution for the powdered samples. This saturation value will probably be a function of pH and so one would not expect the solid sample leach solutions to reach these values

unless the pH was comparable. Thus, it is not clear that powder leach samples give results which can be intelligently used to predict solid sample leach behavior. The leach solution analyses for both powdered and solid samples are given in Exhibit 4.

The leaching behavior of 7668 glass and a supercalcine ceramic in a gamma-irradiation field have been investigated at a dose rate of 2.4×10^6 R/hr for 309.5 hr to yield a total gamma-irradiation dose of 7.4×10^8 R. This dose rate is representative of that found in encapsulated commercial waste of relatively new vintage. The temperature gradient in the sample holder was 7°C which yielded leach temperatures from 85° to 92°C depending upon sample location. All SA/V ratios were 0.10 and the leach solutions were distilled water and a mild saltwater solution (700 ppm Na).

Elemental analyses of the leach solutions for the irradiated and unirradiated samples are given in Exhibit 5. A direct comparison can only be made for the distilled water leach solution. It is interesting that the leach solution pH change in gamma-irradiated samples is small compared to unirradiated samples. It can be concluded from the results on Exhibit 5 that gamma-irradiation has significantly increased the elemental leaching for both 7668 glass and supercalcine ceramic. Additionally, the distilled and saltwater leach solutions resulted in somewhat similar leaching behavior during gamma-irradiation. The data in Exhibit 5 can be presented in a different form by normalizing to the amount of element originally present, the surface area, and the leach time. This results in fraction leached per unit area and time or a leach rate. These results are tabulated in Exhibit 6 along with the standard way (weight loss) of presenting leach rate results. The weight loss technique gives trends but no real information. It can be seen from Exhibit 6 that the gamma-irradiation significantly increases the leach rates of most elements in the sample material.

These results have stimulated enough interest that temperature and dose rate dependencies are currently being investigated.

EXHIBIT 1. Elemental Concentrations in the Distilled Water Leach Solutions for Solid 7668 Glass Samples

EXHIBIT 2. Fraction of Original Elemental Concentration Removed by Leaching in Distilled Water per Unit Surface Area of Sample for Solid 7668 Glass Samples.

EXHIBIT 3. Fraction of Original Elemental Concentration Removed by Leaching in Distilled Water per Unit Surface Area of Sample for Powdered 7668 Glass Samples

EXHIBIT 4. Analyses of Leach Solutions for Unirradiated 7668 Glass

Element	Powder (-200 mesh)					Solid Samples			
	17.5 hr	65 hr	138 hr	237 hr	477 hr	27 hr	119.5 hr	218.5 hr	459 hr
Si	410.3 ^(a)	176	143	155	79	5	14	15.8	28.3
B	179.3	176	198	205	212	0.9	2.7	3.1	6.5
Al	6.6	0	0	0	0	0.1	0	0	0
Ca	25.3	0	0	0	0	0.4	1.1	1.2	0.5
Sr	5.06	0	0	0.1	0	0.1	0.3	0.3	0.2
Ba	6.6	0.1	0	0.1	0	0.1	0.2	0.1	0
Na	715	539	572	781	935	2.6	7.7	13	27
Cs	--	17.6	7.4	--	4.5	--	2.2	2.1	1.8
Fe	8.8	0	0	3.3	1.1	0	0	0	0
Mo	80.3	78.1	88	91.3	103.4	0.4	1.4	1.7	3.9

^(a) Numbers are in ppm.

EXHIBIT 5. Comparison of Gamma-Irradiated and Unirradiated Leach Results in Distilled Water at Approximately 90°C for 309.5 hr with a V/SA Ratio of 10/1

Element	γ -Irradiated ^(a) 7668 Glass		Unirradiated 7668 Glass	γ -Irradiated Supercalcine		Unirradiated Supercalcine
	SW ^(b) (85°C)	DIW ^(c) (87°C)	DIW (89°C)	SW (90°C)	DIW (92°C)	DIW (89°C)
Si	29.5(d)	40.5	21.0	7.6	10.6	5.0
B	6.0	7.9	4.6	1.3	1.3	0.4
P	<1	<1	0.1	<1	<1	<0.05
Al	<1	<1	<0.1	<1	<1	0.2
Ca	4.6	4.3	1.0	2.8	1.8	0.2
Sr	0.6	0.7	0.2	4.0	4.1	0.8
Ba	0.5	0.7	0.1	3.0	3.0	1.2
Mg	<0.5	<0.5	<0.05	<0.5	<0.5	0.2
Li	<0.5	<0.5	<0.05	<0.5	<0.5	<0.05
Na	—	60.4	18.5	—	29.1	3.8
Cs	1.5	1.8	2.2	1.2	2.7	3.2
Mo	2.7	4.0	2.6	10.9	16.6	3.0
Fe	<1	<1	<0.1	<1	<1	<0.1
Co	<0.1	<0.1	<0.01	<0.1	<0.1	<0.1
Ni	0.3	0.4	<0.01	0.4	0.4	<0.1
pH initial/final	6.6/6.5	5.9/6.5	5.9/8.5	6.6/5.2	5.9/6.0	--

(a) Dose rate was 2.4×10^6 R/hr, total dose was 7.4×10^8 R.

(b) Saltwater solution (700 ppm Na).

(c) Deionized water.

(d) All numbers are ppm.

EXHIBIT 6. Fractional Leach Rate

Element	7668-SW γ -irradiation (cm ² hr) ⁻¹	7668-DIW γ -irradiation (cm ² hr) ⁻¹	7668-DIW no-irradiation (cm ² hr) ⁻¹	SC-SW γ -irradiation (cm ² hr) ⁻¹	SC-DIW γ -irradiation (cm ² hr) ⁻¹	SC-DIW no-irradiation (cm ² hr) ⁻¹
Si	1.67 x 10 ⁻⁵	2.27 x 10 ⁻⁵	6.53 x 10 ⁻⁶	1.03 x 10 ⁻⁵	1.48 x 10 ⁻⁵	3.24 x 10 ⁻⁶
B	2.15 x 10 ⁻⁵	2.80 x 10 ⁻⁵	9.50 x 10 ⁻⁶	--	--	--
Ca	3.39 x 10 ⁻⁵	3.14 x 10 ⁻⁵	4.41 x 10 ⁻⁶	2.09 x 10 ⁻⁵	1.38 x 10 ⁻⁵	4.10 x 10 ⁻⁷
Sr	1.87 x 10 ⁻⁵	2.15 x 10 ⁻⁵	4.89 x 10 ⁻⁶	2.04 x 10 ⁻⁵	2.15 x 10 ⁻⁵	1.97 x 10 ⁻⁶
Ba	9.98 x 10 ⁻⁶	1.38 x 10 ⁻⁵	1.16 x 10 ⁻⁶	1.50 x 10 ⁻⁵	1.54 x 10 ⁻⁵	3.05 x 10 ⁻⁶
Na	--	6.64 x 10 ⁻⁵	1.22 x 10 ⁻⁵	--	2.26 x 10 ⁻³	9.50 x 10 ⁻⁵
Cs	1.53 x 10 ⁻⁵	1.83 x 10 ⁻⁵	1.27 x 10 ⁻⁵	3.1 x 10 ⁻⁶	7.15 x 10 ⁻⁶	5.05 x 10 ⁻⁶
Mo	1.76 x 10 ⁻⁵	2.58 x 10 ⁻⁵	2.67 x 10 ⁻⁶	2.23 x 10 ⁻⁵	3.51 x 10 ⁻⁵	5.33 x 10 ⁻⁶
Ni	1.91 x 10 ⁻⁵	2.53 x 10 ⁻⁵	--	2.85 x 10 ⁻⁵	2.93 x 10 ⁻⁵	--
wt loss	$\frac{8.45 \times 10^{-5} \text{ gm}}{\text{cm}^2 \cdot \text{day}}$	$\frac{1.23 \times 10^{-4} \text{ gm}}{\text{cm}^2 \cdot \text{day}}$	$\frac{5.89 \times 10^{-5} \text{ gm}}{\text{cm}^2 \cdot \text{day}}$	$\frac{9.35 \times 10^{-6} \text{ gm}}{\text{cm}^2 \cdot \text{day}}$	$\frac{3.74 \times 10^{-5} \text{ gm}}{\text{cm}^2 \cdot \text{day}}$	--

LEACHING CHARACTERISTICS OF ACTINIDES FROM SIMULATED
REACTOR WASTE GLASS

by

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INTRODUCTION

This investigation is conducted for the Office of Nuclear Waste Isolation through Task 2 of the PNL Waste Isolation Safety Assessment Program (WISAP). One of the important goals of this program is to be able to calculate the rate of radionuclide release from candidate waste forms for geologic repository disposal.

The present study has the following objectives in support of that goal:

- To provide radionuclide source term information for use in release consequence analysis and migration rate calculations. This includes the effect of leaching, solution composition, flow rate, temperature, and time on the leach rate of simulated high level reactor waste glass.
- To compare results obtained from the dynamic one-pass leaching method at LLL with those from the IAEA method at PNL.

This progress report includes results to 120 days. Additional reports will be issued as the results are analyzed statistically, and a final report will be issued with PNL after the end of the experiments.

(a) Battelle Pacific Northwest Laboratories, Richland, WA 99352.

EXPERIMENTAL WORK

As shown in Exhibit 1, LLL uses a statistically designed factorial experiment with unequal replication. Leach rate is the dependent variable; and solution composition, flow rate, temperature, and time are the independent variables. The study extends from 1 to 420 days; each of the 28 simultaneous experiments is sampled at 11 times during this interval. The PNL experimental design is a modification of the IAEA method in which monthly sampling continues indefinitely.⁽¹⁾ Also, PNL experiments are triply replicated. Both PNL and LLL use the same waste form, the same leaching solutions, and the same low temperature, 25°C. The PNL simulated reactor waste is a sodium zinc borosilicate glass (76-68) in the form of hemispherical beads about 8 mm in diameter. The composition is like that of fully radioactive waste, except for the substitution of nonradioactive fission products. The radionuclides are $^{238}\text{U}_3\text{O}_8$ (4.2 w/o), $^{237}\text{NpO}_2$ (0.46 w/o), and $^{239}\text{PuO}_2$ (0.046 w/o). The leachant solutions are distilled H_2O , 0.03M NaHCO_3 , and synthetic WIPP "B" brine.

The LLL results will be analyzed statistically by fitting the leach rate (R) as a function of time (t) to the model:

$$R = \alpha + \beta t^{-\gamma/2} + \delta \quad (1)$$

where the parameters α , β , γ are functions of the experimental variables temperature, flow rate, and solution composition; and the error term is δ . The effect of the experimental variables on the model parameter will be explored using statistical analysis of variance methods.

SYNOPSIS OF TALK BY D. COLES AT WISAP
TASK 2 MEETING, SEATTLE, MAY 24-25, 1979

Exhibit 2: Status of Bead Leach I Analyses as of 5/17/79.

All samples of the bicarbonate and distilled water have been prepared and counted through day 120. 100 λ of each sample (channels 10-28 for each sample day) was evaporated on a Pt disc, fired in a Meeker burner, and α -counted. Since leach rates generally decrease with time with accompanying decreases in actinide content in the leachate, count times must be increased with the longer time samples. We suspect that for samples collected on days 230 and 420, radiochemical purification of 10 mls will be required rather than simple evaporation of 100 λ . Also, twice as many α -countings are required since Np and Pu are separate samples after radiochemical purification. After evaporations, both actinides can be counted on the same Pt disc.

The radiochemical purification procedure for the brine samples (channels 1-9) have been completed through day 120. The α -counting for both Np and Pu has been completed through day 68.

No ICP analyses have been done on leachate samples. However, calibration studies have been finished in preparation for leachate analyses.

Exhibit 3: Composition of 76-68 Glass and Detection Limits for ICP Analysis of Leachate

This slide shows the elements which the ICP-emission spectroscopy equipment at LLL can observe in water samples and the composition of 76-68 glass. Those elements in common are denoted with an arrow. Analysis for Zr is currently incorrect but the analyses for the other elements is a routine operation with this equipment.

Exhibits 4-6: Acid Calibration Data for ICP Analysis (Replicate Runs of a Standard Solution in Ultrex HNO₃.)

Since the leachate samples had been previously acidified to 6-8 N HNO_3 in order to stabilize Np and Pu in solution, it was necessary to calibrate the ICP equipment for acidified samples. Two independent preparations of a well known standard were done by mixing the standard with Ultex HNO_3 at different normalities. These samples were then analyzed and the data compared to the known value for the standard. The calibration plots shown present the percent deviation of the acidified standard from the unacidified standard as a function of acid normality. The "X" and "O" represent data from both preparations. Excellent agreement can be seen for all elements except Cd. The "O" data for Cd does not fall on the line described by the "X" data. Molybdenum is the only element showing a positive deviation from the known standard. All other elements indicate that increasing acid concentration tends to mask the element in the solution.

Since the precision of these two runs is so good, we feel confident that by diluting the leachate samples to 4N and applying a correction factor based on these calibration curves, we can obtain correct values for the concentrations of these elements in the leachate. So far this can only be done for the bicarbonate and distilled water as the high salt content of the brine prohibits analysis. The ICD people (particularly Art Langhorst) are working on this problem.

RESULTS

Preliminary results are presented here without statistical analysis. For the first 120 days, $\log R$ vs. $\log t$ is shown in Exhibits 7-13. Exhibit 7 shows the coordinate system which applies to Exhibits 8-13 and also shows how the PNL data taken at various sampling intervals correspond with subsets of the LLL 25°C data at fast, medium, or slow flow rates. In Exhibits 8-13, the full lines correspond to 25°C, the dotted lines to 75°C, and F, M, S, to fast, medium, and slow flow rates, respectively. In each exhibit, the blank is shown by a dashed line. The PNL results obtained by their modified IAEA method are shown as filled circles.

The range in leach rates is from 2×10^{-4} to 2×10^{-7} g/(cm².d) for ²³⁷Np (Exhibits 8-10) and from 2×10^{-5} to 2×10^{-9} g/(cm².d) for ²³⁹Pu (Exhibits 11-13). Leach rate usually decreases with time, but at high temperature the time dependence is usually smaller than it is at room temperature. At high temperature, leach rate increases with flow rate for all solutions and both radionuclides. At room temperature, leach rate is approximately independent of flow rate; this will be checked for statistical significance during analysis. High temperature leach rates are greater than those at room temperature for ²³⁷Np, but less than or equal to those at room temperature for ²³⁹Pu. As indicated in Exhibit 7, the room temperature results for LLL and PNL can be compared directly. Agreement is fair in WIPP brine (Exhibits 10-13) and excellent in distilled H₂O (Exhibits 8 and 11) and NaHCO₃ (Exhibits 9 and 12). Further work on this part of the bead leaching studies includes collection of the final (420-day) effluent sample in June, continuation of data reduction and analysis of the results, and post-run examination of the sample cells and beads.

CONCLUSIONS

Even without statistical analysis, some general trends can be seen in the results:

- Leach rate increases with flow rate at high temperature, but is approximately independent of it at room temperature.
- Agreement between the results from the one-pass method and those from the IAEA method are fair in the case of WIPP brine solution, and excellent in the case of the others.
- The ^{237}Np leach rate increases with temperature, but the ^{239}Pu leach rate either decreases with temperature, or does not change. This low net transport rate is surprising, and we therefore plan to look for ^{239}Pu in various parts of the sample cells in order to determine where it is located in the system.

REFERENCES

1. Hespe, E. D. 1971. Leach Testing of Immobilized Radioactive Waste Solids, A Proposal for a Standard Method. Atomic Energy Review 9:195.

EXHIBIT 1. Experimental Design, Single-Pass Leach System

EXHIBIT 2. Status of Bead Leach I Analyses (5/17/79)

BICARB &
DW
CHANNELS
(10-28)

DAY	1	2	3	6	11	20	34	68	120	230	420
100 λ EVAP. COMPLETED											
α -COUNTING COMPLETED (Np & Pu)											

BRINE CHANNELS
ONLY (1-9)

CHEMISTRY COMPLETED											
α -COUNTING COMPLETED (Np)											
α -COUNTING COMPLETED (Pu)											

ALL
CHANNELS

ICP ANAL.											
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EXHIBIT 3. Composition of 76-68 Glass and Detection Limits for ICP Analysis of Leachate

<u>ICP Detection Limits</u>		<u>Glass Composition Weight Percent</u>	
Al	0.01 µg/ml	0.13	Rb ₂ O
As	0.21	0.38	SrO ←
→ B	0.03	0.21	Y ₂ O ₃
→ Cd	0.003	1.77	ZrO ₂ ←
Co	0.008	2.28	MoO ₃ ←
Cu	0.001	1.07	RuO ₂
→ Fe	0.002	0.17	Rh ₂ O ₃
Li	0.001	0.53	PdO
Mn	0.001	0.03	Ag ₂ O
→ Mo	0.01	0.03	CdO ←
→ Ni	0.01	0.26	TeO ₂
P	0.4	1.03	Cs ₂ O
Pb	0.03	0.56	BaO
→ Si	0.01	0.53	La ₂ O ₃
→ Sr	0.01	1.19	CeO ₂
→ Ti	0.001	0.53	Pr ₆ O ₁₁
→ U	0.04	1.67	Nd ₂ O ₃
V	0.004	0.33	Sm ₂ O ₃
→ Zn	0.005	0.07	Eu ₂ O ₃
→ Zr	0.002	0.05	Gd ₂ O ₃
→ Ca	0.002	4.58	U ₃ O ₈ ←
K	0.2	9.77	Fe ₂ O ₃ ←
Mg	0.001	0.41	Cr ₂ O ₃
→ Na	0.01	0.20	NiO ←
		0.48	P ₂ O ₅
		12.51	Na ₂ O ←
		39.80	SiO ₂ ←
		9.47	B ₂ O ₃ ←
		2.00	CaO ←
		4.97	ZnO ←
		2.97	TiO ₂ ←

Detection limits (based on 4 times the matrix blank).

EXHIBIT 4. Acid Calibration Data for ICP Analysis
(Replicate runs of standard in Ultrex
 HNO_3) - 1

EXHIBIT 5. Acid Calibration Data for ICP Analysis
(Replicate runs of standard in Ultrex
 HNO_3) - 2

EXHIBIT 6. Acid Calibration Data for ICP Analysis
(Replicate runs of standard in Ultrex
 HNO_3) - 3

EXHIBIT 7. Leach Rate Versus Time for LLL and PNL Data.
The general relationship between the two data sets is indicated.

EXHIBIT 8. Neptunium Samples in Distilled Water

EXHIBIT 9. Neptunium Samples in Biocarbonate

EXHIBIT 10. Neptunium Samples in Brine

EXHIBIT 11. Plutonium Samples in Distilled Water

EXHIBIT 12. Plutonium Samples in Bicarbonate

EXHIBIT 13. Plutonium Samples in Brine

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LEACHING PROPERTIES OF SOLIDIFIED TRU WASTE FORMS^(a)
(WBS Element 0206)

by

P. Colombo and R. M. Neilson, Jr.^(b)

PROGRAM DESCRIPTION

Approximately 12×10^6 ft³ of defense TRU wastes are in storage or burial at various DOE installations, principally at the Idaho National Engineering Laboratory (INEL), Hanford, and the Savannah River Plant. (Continued waste generation rates of 2×10^5 ft³/yr are estimated.) These wastes will ultimately be moved and placed into a geologic repository for disposal. While there is some question as to whether existing TRU wastes will be disposed in their current form or first undergo some additional volume reduction process, it is evident that volume reduction will be required for future TRU wastes. Since the bulk of these wastes consists of contaminated combustible solids including such items as protective clothing, rubber boots and gloves, paper, rags, filter aids, wood, and ion exchange resins, volume reduction assumes considerable importance relative to the reduction of waste shipment volumes, conservation of repository capacity, lowering of disposal costs, and meeting repository criteria directed at restricting the amount of combustible material in disposal. There are a number of volume reduction options available for combustible TRU wastes, the most viable option currently being some form of incineration. While incineration does result in a large volume reduction for combustible solid wastes, the ash that results is highly dispersible. As such, the immobilization of incinerator ash by solidification producing a solid monolithic waste form is desirable.

Safety analysis of solidified TRU contaminated incinerator ash waste forms requires an estimate of the ability of these waste forms to retain

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- (a) Presented at WISAP Task 2 Workshop, Battelle Seattle Research Center, May 24-25, 1979.
(b) Brookhaven National Laboratory, Department of Nuclear Energy, Upton, New York 11973.

activity in the disposal environment. The primary mechanism for the potential release of this activity is assumed to be by leaching. The experimental program conducted at Brookhaven National Laboratory will determine the leaching properties of TRU contaminated incinerator ash waste forms using hydraulic cement, urea-formaldehyde, bitumen, and vinyl ester-styrene as solidification agents. The data obtained will indicate the relative activity retention abilities of these waste forms and provide the basis for long-term release projections from full-scale waste forms. The leach rates of the following radionuclides: ^{239}Pu , ^{235}U , ^{237}Np , ^{241}Am , ^{137}Cs , and ^{90}Sr are of interest. Waste form leach rates for these radionuclides will be determined where practical although experimental expediency may dictate the use of other isotopes of these elements and/or availability considerations preclude the use of one or more of these elements.

Three types of leaching tests will be conducted to provide sufficient data for long-term predictions under a variety of conditions. Initially, leaching data will be obtained by use of an IAEA/ISO leach procedure.^(1,2) In this method, the entire external surface area of the waste form is exposed to a leachant solution at 25°C which is sampled and completely replaced at 24-hr intervals for the first 5 days, after which the leachant is replaced once per week for the following 8 weeks and then once per month. Static leach tests will also be performed at both 25°C and 70°C. In these tests, the leachant solution is not changed and is only sampled once. For a given waste form and leachant type, six leach specimens will be prepared (for each temperature) to allow leachant sampling at 2 days, 4 days, 8 days, 16 days, 106 days, and 341 days. The final leaching test procedure will be a flow rate study where activity release will be determined for three leachant flow rates of from 10^{-3} g/min to 1 g/min, which covers the range of observed aquifer flow rates. All leach test procedures will include some replication.

For each of the leaching procedures, five generic groundwaters will be employed as follows:

- 1) Salt brine whose formulation is based on an analysis where a salt rock core taken at the 2725 foot level of AEC 3 at the WIPP facility was dissolved in deionized water. This salt brine composition is shown in Exhibit 1.
- 2) Simplified sodium dominated groundwater, 30 meq/liter NaCl.
- 3) Simplified calcium groundwater, 30 meq/liter CaCl_2 .
- 4) Simplified bicarbonate groundwater, 30 meq/liter NaHCO_3 .
- 5) Deionized water.

WASTE FORM FORMULATIONS

Solidification agents should incorporate relatively as much incinerator ash as possible in the final waste form to maximize packaging efficiency and reduce associated disposal costs. However, the waste form ash content should not be so high as to either impose substantial difficulties in the solidification process or to compromise waste form properties. The amount of ash that can be reasonably incorporated in the waste form is dependent on the composition of the ash and its interaction with the solidification agent. Simulated incinerator ash compositions have been formulated for various waste producing sites. These compositions vary considerably and have been shown to result in different compositional phase diagrams for acceptable solidification with Portland type I cement.⁽³⁾ In addition, simulated waste compositions while similar chemically to actual wastes, may not adequately simulate the physical form or chemical distribution of actual incinerator ash. As such, this program utilizes an actual incinerator ash resulting from the incineration of a mixed combustible waste representative of plutonium handling and processing facilities.

Waste forms are formulated using incinerator ash waste produced by the rotary kiln incinerator at Rocky Flats. This incinerator has been used to burn a nonradioactive mixed combustible waste formulation that is representative of the low level wastes produced at Rocky Flats. The waste feed composition and incinerator operating parameters employed are shown in Exhibit 2. A

40 kg batch of this ash was received at BNL at the end of February 1979. A sample of this ash was taken for analysis by DC arc emission spectroscopy. The results of this analysis and one performed at Rocky Flats are shown in Exhibit 3. For both sets of analyses, confidence limits are approximately $\pm 10\%$ for concentrations above one weight percent and $\pm 50\%$ for lower concentrations (except where indicated). Both analyses are in reasonable agreement. Differences may be due to inhomogeneities in the ash samples analyzed. The ash composition determined from the Rocky Flats analysis has also been used to calculate a cumulative composition weight percentage assuming that cations have been completely converted to stoichiometric oxides. This calculation provides a cumulative composition of 90.7% for all species identified. However, more than one oxidized state may exist for some cationic species. In addition, visual observation of the ash suggests that the ash contains some metallic species in partially unoxidized form.

The rotary kiln ash as received has a low bulk density of approximately 0.23 g/cm^3 . It is flocculent in nature (similar to cigarette ash), gray-white in color but exhibits color gradations and has carbon present as distinct particulate. Small pieces of wire and other partially unburned residues are also present. In the presence of water, the ash has a pH of 5.5-6. The characteristics of the as-received ash are significantly different from the simulated ash composition used previously.

While it was desired to formulate specimens using the rotary kiln ash, a source of activity was needed for the leaching experiments. It was decided to obtain a quantity of dual chamber burner incinerator ash from Rocky Flats for this purpose. This incinerator is used to burn highly contaminated combustibles prior to an acid leaching plutonium recovery operation. Two samples of this ash, with a total mass of 318 grams, was received in March. This ash contains 28.9 grams of plutonium. As indicated in the ash assay shown in Exhibit 4, both ash samples are similar with 94% of the plutonium present (on a weight basis) as Pu-239. A small quantity of Am-241 is present in both ash samples. The total plutonium activity content is 12.38 Ci (0.0389 Ci/g ash), of which 13.4% is Pu-239 and 83.0% is Pu-241. Small quantities of this "hot"

ash are added to the "cold" rotary kiln ash during leach specimen fabrication. This is preferable to the simple addition of plutonium since the plutonium incorporated in the waste form will be in the same chemical and physical state resulting from incineration. The relatively small quantity of "hot" ash used will not appreciably alter the average chemical composition of the incinerator ash incorporated into leach specimens.

Prior to the receipt of the actual incinerator ashes, waste form formulations were investigated using the simulated Rocky Flats plutonium recycle incinerator ash composition shown in Exhibit 5 for solidification with Portland type I cement, urea-formaldehyde, bitumen, and vinyl ester-styrene. Waste forms were produced containing a wide range of ash contents with each solidification agent. These formulations were immersion tested in distilled water 3 months to determine the approximate maximum ash content which resulted in waste forms that would be expected to maintain their integrity during leach testing. An approximate upper limit of 50 wt% simulated ash was found for Portland type I cement, urea-formaldehyde, and bitumen. Vinyl ester-styrene could incorporate 75 wt% ash although some difficulties with its promoter-catalyst system were noted.

Formulational work using the "cold" rotary kiln ash with cement solidification indicated that it behaves considerably different than the simulated ash composition used earlier. This difference is largely attributable to the physical structure of the ash. It has a large particle size with significant contained porosity as indicated by its apparent water absorption. However, the water required to saturate the ash is weakly held since it separates on mixing. The ash as-received is difficult to mix directly with cement (independent of the order of addition) unless sufficient water is added to satisfy the ash's absorptive requirements. When sufficient water is added, a minimum of mixing often resulted in water separation and an excessively wet mixture. To minimize these tendencies, the ash was ball milled. This not only decreased the ash particle size and porosity, but also resulted in a more homogeneous ash with a bulk density of approximately 0.37 g/cm^3 . The resulting ash had lower (although substantial) water requirements for cement

formulations and was also easier to work with. The cement waste form formulation which was developed for the experimental program consists of 30 wt% ash, 30 wt% cement, and 40 wt% water. The ash content of this formulation is lower than that developed for the simulated ash because of the significantly higher water content requirements of the actual ash.

These differences in ash behavior also affect solidification with urea-formaldehyde, bitumen, and vinyl ester-styrene. As such, the "cold" ash will be ball milled prior to incorporation in all binders. The formulation with urea-formaldehyde (UF) is 34% ash, 44% UF, 17% water, and 5% sodium bisulfate catalyst solution by weight. Initial UF leaching specimens did not solidify. This is apparently due to the alkalinity of the "hot" ash, which can be compensated for by the addition of more acid catalyst.

TRU HANDLING AND LEACHING FACILITY

Facility Cell

The transuranic handling and leaching facility has been constructed inside the former Irradiation Cell in Building 830. The inside dimensions of this hot cell are 14'x20'x14' high. The walls are 4-1/2 feet thick, constructed of medium density concrete (240 lb/ft³), with the exception of the wall containing the access door. This wall is 6-1/2 feet thick and is composed of ordinary construction grade reinforced concrete with a density of 150 lb/ft³. The access door, which is lead encased in steel, weighs approximately 25 tons and closes the main cell opening which is 5 ft wide and 7 ft high. Additional access is available through ceiling and wall plugs. The ceiling is made of ordinary construction grade reinforced concrete and is 6-1/2 ft thick. Two cell walls each have a 52-in. thick high density lead shielding glass window. In addition, this cell was equipped with two through the wall manipulators and a completely enclosed General Mills arm manipulator. The Irradiation Cell is connected to an adjacent Preparation Cell by a 16-ft deep water canal.

While the extensive shielding capability provided by the irradiation hot cell is not necessary for the transuranic leaching experiments proposed, the

space was available and it does serve as an effective means of isolating the work from general laboratory facilities. Some modification of the cell interior was required to make this space suitable for a leaching facility. The cell was surveyed to determine the level of existing contamination, if any. No significant contamination was detected (none was expected since the cell was only used for irradiation experiments using sealed sources). The General Mills arm was removed as were two canal elevator lift and transfer assemblies. The elevator openings to the canal and a center floor opening to an enclosed water pool were covered with stainless steel plates. The interior of the cell was then completely repainted. A fire retardant wooden interior doorway was constructed to permit restricting access to the facility during the working day when the lead shielding door is open. While the cell has existing gamma radiation monitoring equipment and alarms, an alpha air monitoring unit was installed (Eberline Model Alpha-3). In addition, both photoelectric and ionization chamber smoke detectors have been installed.

The cell has its own temperature controlled air recirculation system which contains two levels of HEPA filtration. The facility will probably be operated at 100% recirculation although the percentage of air which is recirculated can be varied. Any portion of air which is not recirculated is connected to the main laboratory stack inlet where an air flow rate of 700 linear feet per minute moves the exhaust air to the stack which is approximately 1/4 mile from the inlet. The initial level of HEPA filtration is located at the cell exhaust duct while a second HEPA filter is located in the basement machine room at the main stack exhaust inlet.

Specimen Preparation Glove Box

A two compartment stainless steel glove box with an air lock entry assembly for each compartment has been modified and placed in the leaching facility to provide capability for remote fabrication of transuranic contaminated leaching specimens. This glove box had been previously used at the laboratory for plutonium handling operations. The unit was thoroughly decontaminated prior to receipt in Building 830. Each of the two compartments is 33 in. long x 24 in. wide x 33 in. high. They are separated by a stainless

steel barrier containing an 11-1/2 in. diameter door. Each compartment has lighting, electrical supply outlets and its own internal HEPA filter in addition to a pair of glove ports. There is an airlock assembly for each glove box compartment. The airlocks are 19 in. long x 19 in. wide x 20 in. high. The airlocks are each separated from the main glove box compartments by an 11-1/2 in. diameter door. Both airlocks also have an 11-1/2 in. diameter door to the outside, a pair of glove ports, and a Plexiglas endplate to permit viewing. The glove box is supported on a table assembly which permits adjustment of the glove box height.

Air from the glove box is exhausted through two levels of HEPA filtration. The first level is the internal HEPA filter in each compartment as previously mentioned. These filters are both connected to a double series HEPA filter outside the glove box through a 2-in. diameter manifold. This is in turn connected to an exhaust pipe leading into 4 in. diameter polyethylene flex tubing which is fed through existing ductwork to an exhaust blower in the basement machine room. The blower is not normally used since the main stack supplies sufficient negative pressure for most glove box uses. The glove box is operated under a negative static pressure of approximately one inch of water. A bagging facility is installed on the "hot" side airlock. An air bleed and HEPA filter is used to bring the box pressure to atmospheric when bagging is performed.

Specimen preparation procedures have been developed under which one side of the glove box is treated as a "hot" compartment in which the specimens are fabricated while the other compartment is "cold." The "cold" compartment is used to remove solidified leach specimens from their preparation containers and place them into leach containers. These leach containers must be uncontaminated to allow their removal from the glove box to the leaching apparatus.

Problems were encountered with the operation of the glove box during the preparation of the first set of leaching specimens (ash, cement, and UF). During transfer to the "cold" side of the box (which took place 24 hr after specimen preparation), significant contamination and airborne activity were noted. This was determined by surface smears and air sampling from the "cold"

compartment. Health physics personnel would not permit the removal of the leach containers until the "cold" side of the box was decontaminated. Also, additional modifications to the glove box were required for further operation. The contaminated ash is apparently highly dispersible with minute particles remaining suspended in the air in the "hot" side of the box for considerable periods. Since the glove box was operated under static negative pressure conditions, this airborne contamination was able to move to the "cold" compartment during the transfer operation. The glove box has been modified to allow an airflow from the "cold" side into the "hot" side during transfers and, if desired, during procedures in the "hot" compartment. The exhaust blower on the recirculation air line is used to provide an increased airflow through HEPA filters and into the glove box when this is desired. A small suction hood is also now used over the "hot" container during specimen preparation. Improved in-box decontamination facilities are also being provided. An improved air sampler on the "cold" compartment airlock has been installed.

Leaching Facilities

A semi-automated apparatus has been designed for performing IAEA/ISO leach tests. This technique requires that the leaching solution be changed and completely replaced at frequent intervals (daily for the first week, once per week for the following 8 weeks and subsequently once per month). Since the leachant solutions are expected to contain quantities of plutonium removed from the leach specimens, it was decided to build an apparatus which would require a minimum of direct manual handling of the specimens and solutions. Leaching equipment was designed and constructed to allow the leaching experiment to be performed in the following manner. The leach specimen is placed into a one liter capacity polymethylpentene screw cap container. This material was chosen because it is autoclavable and has a low potential for reacting with and "plating out" species of interest on the container walls. The specimen is supported on a Plexiglas stand which makes essentially the entire surface area of the leach specimen accessible to the leachant. The container is connected to a 1/4 in. OD valved inlet manifold, through which the desired

amount of leachant can be added to any individual leach container. The manifold and 1/4 in. OD ball valves are type 304 stainless steel. A separate inlet manifold is used for each leachant type. The inlet manifold also has a recirculation return line to prevent clogging of the inlet manifold as well as provide a mixing action in the leachant storage container.

Leachant is stored in steel drums with 27 gallon polyethylene liners. A small Flotec gear pump is used to provide the motive force for leachant transfer. After the appropriate period of leaching, the leachant in the leach container is stirred and sampled using an Eppendorf pipette. After sampling, the valve to the exhaust manifold is opened. Since the exhaust manifold is maintained at a negative pressure, opening the ball valve for the desired leach container removes the leachant under a suction action. A teflon suction tube is positioned in the leachant container which allows removal of essentially all of the leachant. The exhaust manifold is 3/8 in. OD type 304 stainless steel which drains to a 40-gal capacity glass-lined mild steel tank with a fluid level indicator. This tank when full can be drained directly into a feed line to a 2,000 gal capacity pair of buried waste holding tanks (outside of Bldg. 830) which are periodically emptied by tank truck. The leachant exhaust manifold leads to a Plexiglas measuring cell apparatus before emptying into the waste holding tank. The measuring cell allows determination of leachant pH, conductivity and (if desired) Eh and oxygen content.

This apparatus may not, however, be compatible with a leach procedure recently proposed for DOE contractors in TRU programs. This procedure requires periodic removal of "plated" activity from the leach container. However, the procedure can be followed using a two container method with somewhat increased handling.

The static 25° leach tests will be conducted at ambient temperature in the leach facility. The IAEA/ISO procedures specify $25^{\circ}\text{C} \pm 5^{\circ}\text{C}$ while ambient temperature in the leach facility is approximately $21^{\circ}\text{C} \pm 1^{\circ}\text{C}$. The facility temperature will be monitored during testing. A specially modified incubator with excellent temperature stability has been ordered for the 70° static leach tests.

LEACHANT ANALYSIS

Quantitative alpha spectrometry typically employs a solid state silicon surface barrier detector to count specimens electroplated onto stainless steel planchets. The resolution of such a detector is of the order of 50 keV which permits simultaneous analysis of alpha emitters with similar energies. However, the sample preparation required in this technique is very labor intensive. The leaching experiments to be conducted at BNL will produce more samples for analysis than can be conveniently prepared in this manner. As such, other analytical techniques were investigated and liquid scintillation counting (LSC) was chosen as the primary analytical technique.

Liquid scintillation counting has been utilized for alpha counting since 1954.^(4,5) This method is attractive due to the ease of specimen preparation, the commercial availability of remote sample changers, and the 100% efficiency usually obtained in alpha counting. (Alpha particles are counted at 100% efficiency in LSC provided the activity is dissolved in the scintillation solution. The efficiency is lowered by a geometry factor if the activity plates out on the container walls or is suspended on a solid matrix.) While energy resolution is not as good as can be obtained with other methods, different alpha emitters can be counted simultaneously provided their respective alpha particle energies are sufficiently different. Peak resolution in LSC is a function of a number of factors but alpha particles of approximately 5 MeV generally can be resolved if peak energy differences are of the order of 0.5–0.7 MeV. As such, some alpha emitting radionuclides may possibly be analyzed simultaneously since appreciable primary particle energy differences exist: ^{239}Pu (5.147 MeV), ^{241}Am (5.482 MeV), ^{237}Np (4.787 MeV), ^{235}U (4.354 MeV).

A Searle Model 6892 automatic liquid scintillation counter was purchased for this program. It employs a bidirectional automatic conveyor sample changer which accepts up to 300 samples. The detector consists of two 2-in. diameter bi-alkali photomultiplier tubes which are situated 180° apart in a metal chamber with specular aluminum reflectors in a 2-in. thick lead shielding housing. There are two variable simultaneous sample analysis channels

with two additional fixed level channels for external standard source (ESR) analysis. Analysis channel baseline and width, counting time, preset count terminators and sample changing mode can be independently determined and incorporated into internally stored program instructions. Data output is through a Teletype Model 43 printer.

EXPERIMENTAL RESULTS

Experiments were initiated to determine the extent of "plate out" occurring for ^{239}Pu in the semi-automated leaching cells. These cells are constructed primarily out of polymethylpentene which was selected for its low "plate out" potential and thermal stability (autoclavable). "Plate out" is expected to be strongly dependent upon the chemistry of the system. As such, experiments were performed using each of the five leachant solutions and each solidification agent, except urea-formaldehyde. One inch diameter x 2-in. long cylindrical specimens of Portland type I cement, bitumen, and vinyl ester-styrene, each containing 50 wt% simulated ash were leached for 3 weeks in 250 milliliters of leachant without leachant renewal. Also leached was a specimen of Portland type I cement (water/cement = 0.3 by weight) containing no ash. In addition to "plate out" experiments, the resultant leachant solutions were also employed in studies to determine counting efficiency and chemical quenching (if any) in LSC analysis.

After leaching, 10 milliliters of each of the solutions (except brine) were placed into 125 ml polymethylpentene containers (of the same manufacturer as the one liter leaching cell containers). The pH of these leachant solutions was determined. The pH range was 7.5-10 for bitumen and vinyl ester-styrene leachants and 12-13 for cement and cement (no ash) specimens. These leachant solutions were then each spiked with 20 lambda of a 0.5 M HNO_3 solution of ^{239}Pu . After a contact time of 18 hours, the leachants were each sampled and counted. A loss of 40-60% of the initially contained ^{239}Pu was observed. Investigation of "plate out" as a function of time was not conducted.

The leachants, prepared as described previously, were used to determine counter efficiency and the stability of counting samples. These leachants should represent worse case situations for the IAEA/ISO test and should contain large quantities of dissolved solids removed from the leach specimens.

Leachant analysis to date has utilized Packard Insta-Gel as the liquid scintillation cocktail. This cocktail is able to form a stable counting media with relatively large quantities of aqueous samples. A 7 milliliter aliquot of each leachant solution was mixed with 10 milliliters of Insta-Gel and allowed to stand for 2 weeks. Stable counting samples were obtained with all leachants except salt brine. While other leachants formed a stable gel phase with Insta-Gel, the salt brine mixture separated into two phases. A stable counting sample was not obtained with as little as one milliliter of brine leachant in 10 milliliters of Insta-Gel. A stable sample was produced using a 1:25 dilution of the brine prior to combining 7 milliliters of diluted brine with 10 milliliters of Insta-Gel. While a sample which separates into two phases can be counted, the counting efficiency can decrease substantially. A low-level x-ray detector will be used for salt brine leachant analysis.

Alpha particles are counted at 100% efficiency in LSC provided the activity is uniformly distributed in the scintillation solution and no chemical quenching effects occur. Counting efficiencies were determined using each of the leachants spiked with americium-241. Seven milliliters of leachant was combined with 10 milliliters of Insta-Gel for each counting specimen. Counting efficiencies were determined relative to the known quantity of americium-241 added to each LSC vial. Salt brine leachant samples (which were unstable, having separated into two phases) exhibited a range of counting efficiencies of 63.7% to 79.6% with an average of 70.0%. The other leachants had an average counting efficiency approaching 100.0%. Some lower counting efficiencies were determined as indicated in Exhibit 6. It is unclear, however, whether the lower calculated counting efficiencies are due to slight chemical quenching effects or pipeting errors. It appears, in most cases, that pipeting error is most likely since lower efficiencies do not seem to be associated with any particular leachant or waste form type.

It was also noted that small quantities of a precipitate were present in leachants derived from Portland cement waste forms. The precipitate quantity varied from 0.08 to 0.47 grams, with the larger precipitate quantities present in the salt brine leachant. This precipitate was collected for analysis to determine whether it is likely to occur in IAEA/ISO leaching experiments and if it may be expected to remove activity from leachant solutions. This precipitate was found to be calcium carbonate. It is not believed that it will remove substantial quantities of plutonium from the leachant.

A set of scoping specimens was prepared for IAEA/ISO leaching at the end of March. These were the first IAEA/ISO leach specimens whose primary purpose was to determine if sufficient activity had been added to leach specimens to allow the desired level of detectability in the leachant. A Portland type I cement specimen and urea-formaldehyde specimen were prepared, each containing 13.5 mCi plutonium, and placed into 500 milliliters of distilled water leachant. In addition two 0.33 gram ash specimens (12.8 mCi) were prepared for leaching. The UF specimen did not solidify due to insufficient catalyst. Contamination of the glove box "cold" side was noted, as previously mentioned, when these specimens in leach containers were to be transferred to the leaching apparatus. Since leachant samples could not be obtained until health physics requirements were satisfied (33 days), the resultant test is actually a static test. Subsequent LSC analysis of the leachants showed a fractional activity release of 1.6×10^{-8} for the cement specimen with 9.4×10^{-7} fractional release for the ash. These correspond to fractional activity release rates of $4.9 \times 10^{-10} \text{ day}^{-1}$, and $2.9 \times 10^{-8} \text{ day}^{-1}$ for the cement and ash respectively. The leachant containers have not been examined for "plate out."

While problems have impeded the initiation of leach testing, it appears that these problems have been solved. It is expected that current scheduling commitments can be met, although it may be useful to put more initial emphasis on the static procedure than the IAEA/ISO method.

REFERENCES

1. Hespe, E. D. 1971. Atomic Energy Rev. 9(1), 195.
2. International Standards Organization. 1977. "Long-Term Leach Testing of Radioactive Waste Solidification Products." Draft Standard ISO/TC 85/SC 5 WG 5 N 22.
3. Neilson, R. M., Jr. and P. Colombo. 1978. Solidification of Simulated Transuranic Contaminated Incinerator Ash Wastes Using Portland Type I Cement. BNL-50854, Brookhaven National Laboratory, Upton, NY.
4. Basson, J. K. and J. Stayn. 1954. Proc. Phys. Soc. London A67, 297.
5. Horrocks, D. L. 1974. Applications of Liquid Scintillation Counting. Academic Press, New York.

EXHIBIT 1. Composition of Salt Brine Leachant
(derived for AEC 8, 2725-ft level core)

<u>Composition (mg/liter)</u>	
NaCl	287,000
Na ₂ SO ₄	6,200
Na ₂ B ₄ O ₇ ·10H ₂ O	16.0
NaHCO ₃	14.0
NaBr	520.0
KCl	29.0
KI	13.0
MgCl ₂	40.0
CaCl ₂ ·2H ₂ O	3,300
FeCl ₃	6.0
SrCl ₂ ·2H ₂ O	33.0
Rb ₂ SO ₄	1.6
CsCl	1.3
Total Dissolved Solids	297.2 g/liter
pH (Adjusted)	6.5

EXHIBIT 2. Rocky Flats Rotary Kiln Incinerator
Ash Operating Parameters

<u>A. Feed Composition</u>	<u>Weight%</u>
Polyvinyl chloride	7.9
Polyethylene	22.8
Neoprene	18.8
Tributyl Phosphate	1.0
Kerosene	9.5
Paper	<u>40.0</u>
	100.0

<u>B. Feed Rate</u>	
Solids	6.8 kg/hr
Liquids	0.45 liter/hr

<u>C. Operating Temperature</u>	
Kiln	1000°C ± 100°C
After-Burner	1400°C ± 100°C

<u>D. Operating Time</u>	
	~ 150 hr

EXHIBIT 3. Rocky Flats Rotary Kiln Incinerator Ash Composition

<u>Constituent</u>	<u>Weight Percentage</u>	
	<u>RF Analysis</u>	<u>BNL Analysis</u>
C	10.4 ± 30	13.1
Al	18	18
Si	15	10
Zn	2.6	2.6
Ti	1.8	4.8
Fe	1.4	0.3
Ca	1.2	5
Ba	0.94	0.1
Mg	0.65	1
Li	0.5	0.001
Cr	0.12	0.05
Na	0.1	0.5
P	0.1	-
SO ₄ ⁻²	0.1 ± 0.05	-
Ni	0.08	0.1
Mn	0.07	0.03
Cl ⁻	0.06	-
Cu	0.05	0.08
K	0.05	0.1
Pb	0.05	0.03
W	0.05	-
Sr	0.02	0.05
Co	0.01	-
Mo	0.01	-

EXHIBIT 3 (contd)

<u>Constituent</u>	<u>Weight Percentage</u>	
	<u>RF Analysis</u>	<u>BNL Analysis</u>
Zr	0.01	-
Cs	< 0.01	-
Te	< 0.01	-
B	0.005	-
Sb	0.005	-
V	0.005	-
As	< 0.005	-
Cd	< 0.005	-
Nb	< 0.005	-
Ge	0.001	-
Hg	< 0.001	-
Sn	< 0.001	-
Ta	< 0.001	-
Th	< 0.001	-
Be	0.0005	-
Bi	< 0.0005	-
In	< 0.0005	-
Ga	< 0.0001	-
Rb	-	< 0.01
Ag	-	0.0005

EXHIBIT 4. Dual Chamber Burner Incinerator Ash TRU Assay

ASH SAMPLE 1

<u>Isotope</u>	<u>Quantity, grams</u>	<u>%Total Plutonium</u>	<u>Activity, Ci</u>
Pu-238	0.002	0.01	3.49×10^{-2}
Pu-239	17.290	93.81	1.06×10^0
Pu-240	1.078	5.85	2.44×10^{-1}
Pu-241	0.057	0.31	6.51×10^0
Pu-242	<u>0.004</u>	<u>0.02</u>	<u>1.56×10^{-5}</u>
Total Plutonium	18.431	100.00	7.85×10^0
Am-241	0.023	-	4.09×10^{-3}

ASH SAMPLE 2

<u>Isotope</u>	<u>Quantity, grams</u>	<u>%Total Plutonium</u>	<u>Activity, Ci</u>
Pu-238	0.001	0.01	1.74×10^{-2}
Pu-239	9.851	98.83	6.04×10^{-1}
Pu-240	0.611	5.82	1.38×10^{-1}
Pu-241	0.033	0.31	3.77×10^0
Pu-242	<u>0.002</u>	<u>0.02</u>	<u>7.79×10^{-6}</u>
Total Plutonium	10.499	99.99	4.53×10^0
Am-241	0.031	-	3.86×10^{-3}

EXHIBIT 5. Simulated Rocky Flats Plutonium Recycle
TRU Ash Composition

<u>Material</u>	<u>Weight Percentage</u>
Al ₂ O ₃	3.69
BaO	0.59
B ₂ O ₃	1.67
CaO	3.64
Cr ₂ O ₃	2.36
CuO	0.64
Fe ₂ O ₃	5.85
PbO	0.54
MgO	2.90
MnO ₂	0.10
NiO	0.50
P ₂ O ₅	0.59
KOH	0.50
PbO ₂	2.61
SiO ₂	45.00
NaOH	0.89
V ₂ O ₅	0.64
SnO	0.15
TiO ₂	2.17
C	25.00

EXHIBIT 6. LSC Counting Efficiency (Am-241)

<u>Leachant</u>	<u>Leach Specimen(a)</u>	<u>Counting Efficiency, %</u>
Salt brine	Portland cement	79.6
	bitumen	63.4
	vinyl ester-styrene	63.7
	Portland cement (no ash)	73.4
Sodium dominated groundwater	Portland cement	91.8
	bitumen	94.1
	vinyl ester-styrene	99.3
	Portland cement (no ash)	100.1
Calcium dominated groundwater	Portland cement	99.4
	bitumen	95.5
	vinyl ester-styrene	102.6
	Portland cement (no ash)	95.3
Bicarbonate dominated groundwater	Portland cement	100.5
	bitumen	102.7
	vinyl ester-styrene	100.3
	Portland cement (no ash)	102.2
Deionized water	Portland cement	101.9
	bitumen	100.7
	vinyl ester-styrene	95.2
	Portland cement (no ash)	102.9

(a) Except where indicated, 50 wt% simulated ash waste.

INPUT FOR WISAP TASK 2 WORKSHOP

by

M. Thomas and L. Pederson

The portion of the WISAP Task 2 that I will discuss is being done in the Surface Science Section of the Materials Department at PNL. The specific objective of our subtask is to determine the mechanism of nuclide leaching from waste forms. The emphasis is on determining elemental profiles/micro-structural changes that control nuclide motion in the waste form during static, flow, and hydrothermal leaching. We will correlate the measured solid-state changes with the leachate analysis. Therefore, our experiments will not be performed independently of the leaching experiments but will be closely related and tied into leaching experiments. We will also be developing a data base for the modeling task.

In addition to the surface science studies being done at PNL, there is a surface science subtask at ANL. ANL will be presenting the detail of their activities later in the workshop. Briefly, ANL will be doing photoelectron spectroscopy on actinide extended x-ray absorption fine structure measurements on these oxides to determine atomic coordination and radial distribution functions. The data generated at ANL will be used by PNL in its studies of the leached waste forms.

Concurrently with our study of the literature, we are developing the capability to do experiments that will provide data for modeling nuclide release from solid waste. A leached glass sample consists of at least four regions that must be investigated: the outermost surface that is in direct contact with the leachate; a hydrated region (gel layer) of some thickness; an interface region between the gel layer and the bulk of the sample; and the bulk. The required information includes the elemental distribution throughout these regions and how the chemistry of the elements changes from one region to another. Much of this information can be obtained by scanning Auger microscopy (AES) and electron spectroscopy for chemical analysis (ESCA or XPS). However, real glass matrices contain many trace elements with concentrations

below the detectability limit of AES and ESCA. A complete experimental capability for studying waste forms should therefore have a secondary ion mass spectrometer (SIMS). SIMS sensitivity exceeds that of AES by a factor of 10 to 10^4 depending on the element. For many elements, SIMS sensitivity is in the ppm range, which makes it ideal for this application. In addition, waste forms are radioactive so the apparatus must be capable of working with hot samples. The experimental apparatus being developed will have all of the above mentioned capabilities.

Surface study of glass, especially complex glass matrices, is in its infancy. Some problems with using charge particle probes for studying glass or any insulating material and complex matrix systems are: charging problems, ionic mobility, varying matrix, unknown sputtering rates, changing sputtering rates, unknown electron escape depths from glasses, and beam induced chemical changes. Techniques have already been developed to minimize some problems. For example, by varying the angle and energy of incident radiation, using a charge neutralizer and proper masking techniques, sample charging can be minimized. Ion mobility can be minimized by cryogenic cooling of the sample. We are developing ways to get around or minimize other problems. Even considering these problems, we believe worthwhile data will be obtained with surface probes.

In addition to the literature search and equipment development, we have been doing some preliminary AES, sputter depth profiling, SIMS, and ESCA studies of leached simulated waste glass. Exhibits 1 and 2 are Auger energy spectra. The elements are identified in each exhibit. Exhibit 1A is the Auger spectrum of the surface of an as-received 7668 leached sample (sample A4 leached in DI water at 89°C for 252 hr). Exhibit 1B shows the spectrum from the same sample after 1.5 hr of Argon ion sputtering (about 1000 Å in depth). Exhibits 2A and 2B show a similar comparison for 3107 glass leached for 2 days at 200°C in DI water. Notice the changes in Ca, Al oxide, Si oxide, and Na peaks. Exhibit 3A to 3D show an argon ion sputter depth profile for this sample. The ordinate is in atomic percent and the abscissa in sputtering time and approximate depth. Note the changes in the ordinate scale factor for different elements. Exhibit 3A also contains a hydrogen profile taken with

SIMS. The hydrogen profile is similar to that of the silicon and may be associated with the silica gel. After the rapid change in hydrogen and silicon, calcium, iron, and boron continue to change to a depth of 200 minutes of sputtering time ($\sim 2000 \text{ \AA}$). At this depth sodium becomes detectable. These profiles show considerable elemental variation with depth which is related to atom motion during leaching. Exhibits 4A and 4B are ESCA scans from a leached 3107 glass. Exhibit 4A shows top surface of the sample and Exhibit 4B shows a scan after 200 $\text{\AA}$ of the surface have been removed. Notice the large change in the Fe_{2p} peaks, indicating a change in the Fe chemistry. Exhibits 5A to 5E show positive SIMS spectra of 7668 glass with a trace of UO_2 added. The purpose of showing these spectra is to demonstrate that with SIMS all components in the glass, including U, can be detected.

In summary, our subtask is well under way. The required apparatus are on order and we have shown the usefulness of these techniques on simulated waste samples. Our near-future goals are to determine the sputter rates on these simulated waste glasses. We also will be expanding our data base on leached samples. In particular, we will be measuring samples from static leached tests with varying leaching times.

Following the exhibits is a summary of the viewgraphs used during the workshop presentation.

EXHIBIT 1. Auger Spectra of 7668 Glass, a) leached 254 hr at 89°C as received, b) sputtered to depth of 1000 Å.

EXHIBIT 2. Auger Spectra of 3107 Glass, a) leached at 200°C for 2 days as received, b) sputtered to depth of 500 Å.

EXHIBIT 3A THRU 3D. Sputter Depth Profile of 3107 Glass Leached for 2 Days at 200°C. Note different scale factors of different elements.

EXHIBIT 4. ESCA Spectra of 3107 Glass, a) leached, as received,
b) sputtered to depth of 200 Å.

EXHIBIT 5. Positive SIMS Spectra of Bulk 7668 Glass
a) 0-50 amu, b) 50-100 amu.

EXHIBIT 6. Positive Spectra of Bulk 7668 Glass, c) 100-150 amu, d) 150-200 amu, e) 200-250 amu

SURFACE STUDIES

PNL

by

M. Tom Thomas and Larry Pederson

CONTENTS

Objectives of subtask

Approach to meet these objectives

Discuss preliminary data

- Two glass compositions
- AES
- SIMS
- ESCA

Summary

- Where we are now
- near term goals

OBJECTIVES

Determine mechanisms of nuclide leaching from waste forms

- static
- flow
- hydrothermal

Correlate solid-state changes with leachate analysis

Develop data base for modeling task

APPROACH

Review current state of

- Surface science of glass surfaces
- Leaching data - from glass solid point of view

Develop experimental capability

- Elemental distribution (x, y, z)
 - AES
- Chemistry
 - ESCA (XPS)
- Trace element detection
 - SIMS
- Radioactive samples
- Atomic geometry (EXAFS)

Develop measurement techniques to examine glass samples

- Charging problems
- Ionic mobility
- Varying matrix
- Unknown sputtering rates
- Changing sputtering rates
- Electron escape depths unknown from glasses
- Chemical changes (beam)

Develop model for release from solid waste form

SUMMARY

Where are we now

- Review well under way
- Experimental apparatus on order
- Preliminary data from leached simulated waste glass

Near future goals

- Determine sputtering rates
- Expand our data base on leached glasses
 - static
 - varying leaching times

X-RAY PHOTOEMISSION SPECTROSCOPY (XPS) AND EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) STUDIES OF SILICATE BASED GLASSES

by

D. Karim and D. J. Lam

XPS STUDIES

The application of the XPS technique to study the electronic structure and bonding of heavy metal oxides in alkali- and alkali-earth-silicate glasses had been demonstrated.⁽¹⁾ The bonding characteristics of the iron oxide and uranium oxide in sodium silicate glasses were deduced from the changes in the oxygen 1s levels and the heavy metal core levels. It is reasonable to expect that the effect of leaching on the heavy metal ions can be monitored using the appropriate core levels of these ions. To study the effect of leaching on the glass forming network, it is necessary to monitor the valence band structure of the "bridging" and "nonbridging" oxygens themselves. We have investigated the valence band structure of the "bridging" and "nonbridging" oxygens in sodium disilicate glasses. The electronic structure of "bridging" and "nonbridging" oxygens deduced from the sodium disilicate glass are shown in Exhibits 1 and 2. The XPS spectra are compared with the local density of states at the oxygen sites obtained from a tight-binding calculation⁽²⁾ (Exhibit 3). The combination of theory and experiment enable us to identify the "bridging" and "nonbridging" oxygen in the valence band region and the composition of the molecular orbitals. By carefully monitoring the changes in the valence band and the core levels of the "bridging" and "nonbridging" oxygens, the changes in sodium concentration and the oxygen-silicon ratio, we should be able to obtain information on the effect of leaching on the glass forming network.

EXAFS STUDIES

The measurement of extended x-ray absorption fine-structure (EXAFS) is a relatively new analytical technique for obtaining short range (<5 Å) structural information around atoms of a selected species in both solid and fluid

systems. We have recently begun experiments to establish the feasibility of using EXAFS to study the bonding of actinides in silicate glasses. We feel that, because of the ability of EXAFS to yield specific structural data even in complex multicomponent systems, it could prove to be an invaluable tool in understanding glass structure. Utilization of the technique requires knowledge of k -dependent phase shifts and scattering amplitudes for the atoms involved and they are usually obtained by examination of EXAFS spectra on systems of known structure. Before our study began, little if any work had been done on elements heavier than gold.

Using a rotating anode x-ray source, we have obtained EXAFS spectra above the uranium L_{III} edge (17.165 keV) in several compounds of known structure such as the intermetallic compounds UAs and UGe_3 . These compounds were chosen for the preliminary studies because of their simple crystal structures and moderately heavy backscattering atomic species (the fine structure has a greater amplitude for high Z backscatters). The EXAFS spectra $\chi(k)$ of UGe_3 are shown in Exhibits 4, 5, 6 and 7. Very good signal-to-noise ratio can be obtained on the uranium- and germanium-edge. The Fourier transform of $\chi(k)$ shows the "radial distribution function" at the uranium and germanium sites. From the known UGe distance and the number of near-neighbor in this compound, we can obtain information about the EXAFS parameter $f(k)$ and $\phi(k)$ which are necessary for analyzing the uranium EXAFS results obtained from samples with unknown structure. We are extending these measurements to systems in which the valence and chemical environment of the uranium atoms is more similar to that of uranium in silicate glasses (e.g., UO_3).

Structural information contained in EXAFS data may also be of significant value in determining the form in which the actinides exist in leach solutions (e.g., whether or not the actinide ions are still associated with other atoms from the glass matrix). This information in turn would be most helpful in determining the actual leaching mechanism. For dilute samples, a substantial signal-to-noise improvement in EXAFS spectra is obtained when the absorption coefficient is measured via fluorescent re-emission of the absorbing atoms. In order to obtain the sensitivity limits of this technique as applied to the

leaching problem, we examined a 0.02 molar aqueous solution of uranium nitrate. An overnight run yielded an EXAFS spectra with reasonable signal-to-noise ratio. We have estimated that with the photon flux available in our laboratory, our present technique is usable on uranium solutions down to 0.005-0.01 molar. Another order of magnitude dilution should be attainable with detectors capable of discriminating against higher energy photons Compton scattered from the water. We plan to test this extension of the technique using a solid state germanium detector. Two to three orders of magnitude in sensitivity can be obtained with synchrotron light source with good filtering system.

The fluorescent detection scheme can be made surface sensitive by hitting the sample at a glancing angle and absorbing the x-rays in the uppermost few microns. We have tested this technique using a $\text{Na}_2\text{O} \cdot 2\text{GeO}_2$ glass and a germanium substituted sodium disilicate glass with 10% Fe_2O_3 . Preliminary results indicated that the fluorescent mode is much inferior to the transmission mode for the solid sample. Experiments are still in progress with the aim to improve the glancing angle technique for surface study.

In summary, the XPS technique can be applied to study the electronic structure of the heavy metal ions and the glass forming network of silicate glasses. The glass-water reaction can be monitored by this technique but very long and careful experimental work is anticipated. It has been established that the EXAFS technique can be applied to actinides. In our opinion, it may well be one of the most powerful tools for the speciation study. However, this may require a close collaboration of a clever EXAFS experimentalist and a very good solution chemist in order to do a creditable job.

REFERENCES

1. Lam, D. J., B. W. Veal, H. Chen and G. S. Knapp. 1978. "Bonding of Metal Oxides in Sodium Silicate Glass." In Proceedings of the Symposium on Science Underlying Radioactive Waste Management, Boston, MA, November 28-Dec. 1.
2. Chadi, D. J., R. B. Laughlin and J. D. Goannopoulos. 1978. "Electronic Structures of Crystalline and Amorphous SiO_2 ." In Proceedings of the International Conference on Physics of SiO_2 and Its Interfaces, p. 55. Pergamon Press, New York.

EXHIBIT 1. XPS Spectra of (a) $(\text{Na}_2\text{O})_{0.158}(\text{SiO}_2)_{0.842}$ and
(b) $(\text{Na}_2\text{O})_{0.495}(\text{SiO}_2)_{0.505}$ in the Valence Band Region.

Fourfold magnification of the spectra within 15 eV of E_F is shown in the insert.

EXHIBIT 2. Difference Spectra of Exhibit 1 (a) Is the Difference Spectrum of Exhibit 1a and 1b After the Silicon Is Subtracted Out and (b) Is the Difference Spectrum of Exhibit 1a and 1b and Exhibit 2 After the Sodium Is Subtracted Out

EXHIBIT 3. Comparison of Experimental and Theoretically Calculated XPS Spectra of "Nonbridging" Oxygen (a) and "Bridging Oxygen" (b)

EXHIBIT 4. Normalized EXAFS Above the Germanium K Edge in UGe_3 .

EXHIBIT 5. Fourier Transform of UGe_3 Germanium K Edge EXAFS Data from Exhibit 4.

EXHIBIT 6. Normalized EXAFS Above the Uranium L_{III} Edge in UGe_3 .

EXHIBIT 7. Fourier Transform of UGe_3 Uranium L_{III} Edge EXAFS Data from Exhibit 6.

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LEACHING U-Np-Pu-LOADED SIMULATED WASTE-GLASS

by

Herbert Diamond and A. Friedman

SUMMARY

Static leaching measurements were made in an oxygen-free environment. Three solutions, water, 0.3 M NaHCO_3 and brine were used; three intervals 2d, 8d, and 32d, and 23°C and 75°C temperatures were examined. The preliminary results show a varied response to temperature and some evidence that the leached material is not bound in siliceous fragments.

EXPERIMENTAL

The flow of samples is apparent in Exhibit 1. The use of a 134cc Ge(Li) γ -counter assures that any ^{237}Np (87 keV) or Pa^{233} (312 keV) would not escape notice. Alpha-counting is less secure in this respect.

Alpha-counting and pulse analyses were possible by direct sampling of water and 0.03 M NaHCO_3 solutions. The plutonium in the brine solution was determined by isotopic dilution and pulse analysis. Any plutonium deposited on the secondary container wall would be missed.

The uranium (and other elements found in the water-leach solution) was determined by neutron activation analyses by Edmund A. Huff. The recovery of uranium from brine and NaHCO_3 is indicated in Exhibit 2. The scheme chosen allowed any UO_2^{++} trapped in a siliceous matrix to be dissolved, reduced, and precipitated. Blanks showed no uranium (<5 ngm).

Oxygen was excluded by bubbling N_2 ($<10^{-6}$ atmospheres of oxygen) through the leach-solutions. This procedure was limited in NaHCO_3 because the loss of CO_2 raised the pH. The room-temperature samples remained in a dry-box (about 10^{-5} atmospheres O_2); the 75°C samples were put into mason jars, and these went into pressure cookers having a provision for maintaining a flowing N_2 atmosphere; these went into ovens. The heated samples eventually reached atmospheric pressure; there was a small loss of water vapor.

RESULTS AND DISCUSSION

The activity found in leach solutions, in the scrub solutions, and the minor amounts left on the walls after scrubbing were all summed and reported in Exhibit 3. The numbers are derived from the total amount of material removed from the glass divided by the weight fraction of that material within the glass, and divided again by 4.5 cm^2 (the assumed exposed area of glass). Each number is the result of a single measurement of each of the components; where redundancy existed (neptunium analyses) agreement was satisfactory.

Though the data for samples 2 and 8 indicate less leaching for the longer exposure, a subsequent γ -analysis of the spent beads showed that they were very much alike in neptunium content.

Exhibit 4 shows the leaching of other glass components into water. The behavior of cesium is similar to that of sodium for 75°C solutions, but it differs at room temperature.

The scrub solutions (HNO_3 -HF, 3 hours of vigorous shaking) contained large amounts of plutonium and less of neptunium. The fractionation of plutonium and neptunium (Exhibit 5) implies that they are not locked together in fragments of glass, such as have been observed elsewhere.⁽¹⁾ Much more striking is the fractionation of ^{237}Np from its 27 day daughter ^{233}Pa . For the most part, the protoactinium does not leave the bead. Though it is clearly seen with the neptunium, most of it has grown in after the neptunium has left the bead. This provides a clear case of atom-by-atom crossing of a phase-boundary. (Exhibit 6.)

NEW DIRECTIONS

1. Silica analyses may help understand these data.
2. XPS observations⁽²⁾ have indicated a uranium-iron glass may have UO_3 in separate domains and iron in specific silica-lattice sites. This ought to be reflected in very high U/Fe ratios in a leaching experiment.

3. Speciation studies require that the solution be experimentally tractable. The CO_3 , HCO_3 systems seem ready for study. Amine extraction can probably be developed into a speciation tool that does not markedly disturb the solution being measured.⁽³⁾ Current studies at Argonne can provide starting carbonate and bicarbonate solutions of actinides that are spectrally and potentiometrically characterized.

REFERENCES

1. Scheffler, K., V. Riege, K. Louwrier, H. Matske and H. Thiele. 1977. "Long-Term Leaching of Silicate Systems: Testing Procedure, Actinides Behavior and Mechanism." KFK 2456 or EUR 5509E.
2. Lam, D. J., B. W. Veal, H. Chen and G. S. Knapp. 1978. "Bonding of Metal Oxides in Sodium Silicate Glass." In Proceedings of the Symposium on Science Underlying Radioactive Waste Management, Boston, MA, November 28-December 1.
3. Veno, K., and A. Saito. 1971. Anal. Chim. Acta. 56, 427.

EXHIBIT 1

EXHIBIT 2. Recovery of Uranium from Brine and NaHCO_3

5 ml Sample

Acidify, HCl

Reduce, Ti^{+3}

Carrier, Tm^{+3}

Add HF and stand 20 min, 50°C

Dissolve in 2M AlCl_3 , make solution 5M HCl , to column

Column: 20% $\text{TCMA}\cdot\text{Cl}$ (aliquot-336) on cellite

Feed and wash: 5M HCl

Elute: 0.5M HNO_3

Recovery: 98%

Recovery by a reverse strike upon UO_2^{+2} in F^- solution

Reduce: Ti^{+3}

Add: Tm Carrier

Recovery: 90%

EXHIBIT 3. Removal of Glass-Bead Surface, Assuming Uniform Dissolution;
in $\mu\text{gm}/\text{cm}^2$. Oxygen has been excluded.

No.	Temperature °C	Solvent	Exposure Time	Np	Pu	U(a)
1	23	water	2d	6.4 ± 0.7	0.85 ± 0.05	0.90
2	75	water	2	7.6 ± 1.4	1.07 ± 0.04	4.2
3	23	0.03 M NaHCO_3	2	13 ± 5	3.9 ± 0.6	0.3
4	75	0.03 M NaHCO_3	2	34 ± 7	2.5 ± 0.1	14.5
5	23	brine	2	2.3 ± 0.2	1.35 ± 0.04	0.54
6	75	brine	2	46 ± 3	1.42 ± 0.06	0.32
7	23	water	8	10.5 ± 0.9	1.31 ± 0.03	
8	75	water	8	1.07 ± 0.25	0.54 ± 0.03	
9	23	0.03 M NaHCO_3	8	2.4 ± 0.2	9.7 ± 0.7	
10	75	0.03 M NaHCO_3	8	6.7 ± 0.4	0.35 ± 0.02	
11	23	brine	8	20.3 ± 2.2	3.0 ± 0.1	
12	75	brine	8	42 ± 3	2.82 ± 0.15	
19	23	water	32	23.5 ± 1.6	0.0303 ± 0.0014	0.45
20	75	water	32	3.5 ± 0.9	1.08 ± 0.06	47.2
21	23	0.03 M NaHCO_3	32	105 ± 3	7.7 ± 0.3	62.7
22	75	0.03 M NaHCO_3	32	2.0 ± 0.2	0.74	(b)
23	23	brine	32	26.8 ± 2.5	1.91 ± 0.07	15.1
24	75	brine	32	89 ± 4	1.68 ± 0.08	4.7

(a) Errors are estimated to be less than 20%.

(b) A single sample yielded 3450; contamination has not been ruled out.

EXHIBIT 4. Removal of Glass-Bead Surface, Assuming Uniform Dissolution in $\mu\text{g}/\text{cm}^2$. These results come from neutron activation analyses of evaporated water solutions.

<u>Solvent Temperature Exposure Time</u>	<u>Water 23°C 2d</u>	<u>Water 75°C 2d</u>	<u>Water 23°C 32d</u>	<u>Water 75°C 32d</u>
Element				
Sodium	36	647	6.95	2877
Iron	75	<75	--	--
Molybdenum	2.3	129	1.9	68.3
Cesium	2.4	480	1.9	2310
Lanthanum	0.67	<0.67	<0.05	0.62
Cerium	1.0	2.1	<0.1	0.6

EXHIBIT 5. Some Activity Deposits Onto Polypropylene Walls

Pu: 14 of 18 cases had more than 20% of total activity on the walls. Of these, 7 cases exceeded 60%.

Np: 4 of 18 cases had >20% on wall.

U: Only one measurement: 2.7% on wall.

Am and Cm: More than 1/2 on the wall; more Cm than Am.

In KFK 2456, Scheffler, et al.; much of the plutonium is caught on a filter.

EXHIBIT 6. Fractionation: Solution-Walls-Beads

- I. $\text{Np}^{237} \rightarrow \text{Pa}^{233} \xrightarrow{27\text{D}}$
- 2D, H₂O, room temperature
- Np/Pa > 50 times equilibrium value
- More than 20% of Pa (other than that grown in) is seldom seen.
- Apparently, the Pa never leaves the bead, or reabsorbs onto it
- II. As much as 80% of the Pu absorbs on the wall while Np remains in solution

Therefore, the material does not seem to be tied up in siliceous polymers, as reported by Schiffler, et al.; the behavior is closer to atom-by-atom phase changes.

SPENT FUEL LEACH TESTS

by

Bruce Katayama

This presentation is divided into two parts, pre-WISAP and WISAP. The pre-WISAP leach tests were started before WISAP sponsorship and do not give data directly applicable to the spent fuel release modeling studies being done in WISAP Task 2. However, the general leaching trends have suggested the general approach to some mechanistic studies.

The WISAP portion of this presentation was started under WISAP sponsorship and is designed to fulfill the requirement of obtaining radionuclide release rates from spent fuel and understanding the radionuclide release process under simulated geologic storage conditions.

PRE-WISAP

This portion of the spent fuel leach studies at PNL relate to work started under the Waste Fixation Program in 1975. The experiments were done in Paige leach apparatus as schematically shown in Exhibit 1. These Paige apparatuses were installed in a shielded facility during the Waste Solidification Engineering Prototype (WSEP) program to measure the leach rate of the waste forms produced. The experimental procedures were designed to compare the leachability of solidified waste forms for up to one year of cumulative leach testing. The data presented are for tests extended beyond the one year standard duration and these tests are listed in Exhibit 2.

Exhibit 3 shows the leach rate curves for 54,500 MWd/MTU spent fuel in deionized water at 250°C. Duplicate samples are designated Z-6 and Z-7. The leach rate curves rise and become near equal at about 600 days and then decrease again. Experimental work to understand the leaching mechanism during this period near 600 days is a part of the ongoing oxidation effect studies.

Exhibit 4 shows the cesium based leach rate for 54,500 MWd/MTU spent fuel in deionized water and in a synthetic sea brine at 25°C. The leach rate in deionized water is seven times greater than in sea brine.

Exhibit 5 shows the cesium based leach rate for spent fuels with burnups of 54,500, 28,000, and 9,000 MWd/MTU in deionized water at 25°C. Burnup has no effect on cesium based leach rates.

Exhibit 7 shows the uranium based leach rate for spent fuels with burnups of 54,500, 28,000, and 9,000 MWd/MTU in deionized water at 25°C. The uranium leach rate appears to be dependent on the porosity of the spent fuel (not shown). The 28,000 MWd/MTU fuel is more porous than the 9,000 MWd/MTU fuel.

WISAP

Static leach tests have been started for spent fuel fragments from the H. B. Robinson reactor with a burnup of 28,000 MWd/MTU. The test matrix is shown in Exhibit 8. Tests at 25°C have been started in the container shown in Exhibit 9. The WIPP leachant is a standard WISAP solution of WIPP-B brine.

Oxidation effect studies have been started at PNL. The scouting test matrix (shown in Exhibit 10) is for developing surface analysis techniques. Large single crystal fused UO_2 samples facilitate surface structure analysis. Aerobic conditions will be maintained with an over-pressure of oxygen corresponding to 200 ppm of dissolved oxygen at the test temperatures. Anaerobic conditions will be by outgassing the leachant and purging with argon.

The chemical distribution effect studies have started with the measurement of chemical distribution in the H. B. Robinson fuel (Exhibits 11, 12, 13, and 14). Exhibit 11 shows a cross-section of a fuel fragment and the path of the electron microscope step scan. Exhibits 12, 13, and 14 show the distribution of some of the chemicals along the step scanned path. Note the plutonium concentration gradient and the lack of cesium gradient. This fuel has an average burnup of 28,000 MWd/MTU.

EXHIBIT 1. Paige Leach Test Apparatus

EXHIBIT 2. Paige Leach Tests (25°C)

FUEL BURNUP, MWd/ MT _u	LEACHANTS		
	HANFORD GROUNDWATER	DEIONIZED WATER	SYNTHETIC SEA BRINE
9,000		1977-	
28,200		1977-	
54,500	1975-1976	1975-	1976-

EXHIBIT 3. Extended - Term Leach Rate

EXHIBIT 4. Cesium Leach Rate

EXHIBIT 5. Cesium Leach Rate

EXHIBIT 6. Plutonium Leach Rate

EXHIBIT 7. Uranium Leach Rate

EXHIBIT 8. Static Leach Test

LEACHANT	DAYS						
	2	8	32	106	341	1095	X
WIPP (2)	<div> <div>25⁰C</div> <div>75⁰C</div> <div>28 MWd / kg U</div> </div>						
NaCl							
NaHCO ₃							
CaCl ₂							
DEIONIZED WATER							

EXHIBIT 9. Spent Fuel Static Leach Test Apparatus

EXHIBIT 10. Oxidation Effects - Scouting Tests

SYSTEM	LEACHANT		
	DEIONIZED WATER	WIPP BRINE	NaHCO ₃
AEROBIC	AUTOCLAVE TESTS 75°C, 150°C FUSED UO ₂		
ANAEROBIC			

EXHIBIT 11.

EXHIBIT 12. Microprobe Analysis

EXHIBIT 13. Microprobe Analysis

EXHIBIT 14. Microprobe Analysis

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FUEL AND WASTE IMMOBILIZATION IN CANADA^(a)
RELATED TO WISAP TASK 2

by

G. G. Strathdee^(b), D. J. Cameron, F. P. Sargent, T. T. Vandergraaf
L. H. Johnson, D. W. Shoesmith, P. Taylor,
N. S. McIntyre and J. C. Tait

INTRODUCTION

Several research tasks which are under way in Canada as part of the Concept Verification Phase of the overall Waste Management Program for high-level nuclear fuel wastes are closely related to WISAP tasks. Specifically, we have common interests in improving our understanding of leaching, dissolution, and surface-alteration mechanisms of both spent fuel and high-level waste glass. The results reported here have been obtained within the last 2-3 years and indicate the scope and status of research related to the topic of this WISAP Task 2 workshop.

DISPOSAL OF IRRADIATION CANDU FUEL

The program on packaging of spent CANDU fuel for disposal was described at the recent American Ceramics Society symposium.⁽¹⁾ The experimental studies that are under way are defined by the expected conditions for disposal of spent fuel within our deep (~1 km) hard-rock reference repository. Values for the important variables which affect the experimental program are summarized in Exhibit 1.

It is the exceedingly long thermal period predicted to occur with spent fuel which has focused attention on the long-term durability of this potential waste form. An initial volume-average temperature rise of about 64°C above

(a) Whiteshell Nuclear Research Establishment, Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada, ROE 1L0.

(b) Reported at WISAP Task 2 Workshop, Battelle Seattle Research Center, May 24-25, 1979.

the initial ambient value at 60 yr is due to short-lived fission product decay. A second peak in temperature of about 67°C at 10^4 yr results from decay of long-lived radionuclides. Results are summarized in Exhibit 2 for one case. Note that the volume-average temperature is predicted to exceed $(20 + 55) = 75^\circ\text{C}$ for about 2×10^4 yr. The experimental program on radionuclide loss from spent fuel therefore is concentrated upon performance in the range 75–150°C.

LEACHING OF IRRADIATED CANDU FUEL

Because of the history of this work, which was originally related to durability of stored fuel in water-filled bays, most of the data discussed below has been obtained at about 20°C. However, autoclaves capable of handling up to 1 spent CANDU fuel pin are on order. Initial high-temperature autoclave studies have employed sections of fuel pins, including the Zircaloy cladding for leach rate measurements. This has been necessary because at the normal power rating of CANDU fuel (about 4 kW/m), the UO_2 ceramic is extensively cracked and cannot be reproducibly prepared for leaching.

Irradiated CANDU Fuel Leach Rates at 22°C – T. T. Vandergraaf and L. H. Johnson

Two static leaching experiments using Zircaloy-sheathed sections of Pickering reactor fuel (burnup 610 GJ/kg U) have been in progress for over 900 days. The leach rates of all analyzed radionuclides decreased with time. Results for ^{137}Cs , ^{90}Sr , ^{144}Ce , and Pu (total) are shown in Exhibits 3–6 for both air-saturated distilled and tap water.

The relative rate of activity loss to solution is:

$$^{137}\text{Cs} > ^{90}\text{Sr} > ^{144}\text{Ce} > \text{Pu}$$

The ready leaching of Cs occurs because it is known to migrate radially to the cooler fuel-cladding interface and also to concentrate in cracks in the fuel. The Cs is dissolved readily upon contact with water. In contrast, fission products or actinides which remain in solid solution within the UO_2 matrix are released more slowly to the leachate. The limiting release rate for these

species must be related to the dissolution characteristics of the UO_2 matrix itself. Conversely, the rate of UO_2 dissolution may be estimated by the rate of loss of the rare earth radionuclides (e.g., ^{144}Ce and ^{154}Eu) to solution.

After 600 days of leaching the ^{144}Ce leach rate was less 0.2 ppm/day corresponding to a fuel ceramic leach rate of $6 \times 10^{-6} \text{ g UO}_2/(\text{cm}^2 \cdot \text{day})$. After 900 days this value is less than $0.3 \times 10^{-6} \text{ g UO}_2/(\text{cm}^2 \cdot \text{day})$. Thus, there is some evidence that radionuclide loss is inhibited, perhaps by formation of a passivating surface layer. Electrochemical studies at WNRE have been commenced with the intent of exploring the nature of this surface film (see section by Shoesmith).

The UO_2 dissolution rates estimated from rare earth loss fall within the range of measured uranium dissolution from naturally-occurring uraninite ores. These results are summarized in Exhibit 7. On this scale, our UO_2 -fuel estimates are more comparable to the behavior of relatively pure ore than to those samples containing other elements which may affect the composition and nature of surface-alteration films. A new set experiments has recently been started involving eight samples of fuel in four different simulated-groundwater compositions at ambient temperature, in part to assess the effect of other dissolved species on the characteristics of UO_2 dissolution.

Irradiated-Fuel Leach Rates at 150°C - L. H. Johnson

One piece of fuel has been autoclaved in distilled water in the absence of oxygen for 6 weeks. The ^{137}Cs leach rates were about an order of magnitude higher than under ambient aerated conditions, as shown in Exhibit 8. In contrast, the ^{90}Sr leach rate decreased, as free O_2 was consumed by reaction with the stainless steel autoclave and the UO_2 -matrix dissolution rate was inhibited. Release of alpha-activity was undetectable, but may have been affected by sorption onto the autoclave surface.

Electrochemical Research on UO_2 Dissolution - D. W. Shoesmith

The objective of this work is to understand the mechanism of UO_2 dissolution and to measure the kinetics of dissolution, under groundwater conditions that might be encountered in a hard-rock repository.

Film formation on UO_2 pellets prior to dissolution of uranium as U^{6+} have been investigated using potentiostatic and cyclic voltammetric methods. Results from the former type of experiment are shown in Exhibit 9 as current transients recorded for UO_2 in 0.5 mol/L Na_2SO_4 at different constant potentials and pH values. These observations have been made:

- at low potentials (e.g., 100 mV vs. SCE), a steadily thickening film is produced when the pH is between 3.8 and 10.0.
- at more anodic potential (+ 350 mV vs. SCE) initial film growth is followed by electrochemical dissolution.
- dissolution is greater at lower pH when the potential is + 350 mV.

Voltammetric reduction of the films grown at +350 mV (see Exhibit 10) has confirmed that about 55% of the current contributes to electrochemical dissolution of the oxidized film at pH = 10 compared to 77% at pH = 6.5 and 99% at pH 3.8. The relative dissolution rates of UO_2 under these conditions are 1.0 : 2.1 : 60 at pH values of 10, 6.5 and 3.8 respectively.

The surface film produced on UO_2 has been studied by x-ray diffraction and scanning electron microscopy during controlled electrochemical oxidation. These conclusions have been drawn:

- the main product of UO_2 dissolution (at pH = 9) is hydrated UO_3 .
- the hydrated UO_3 accumulates as a layer on UO_2 , and sediments as a fine powder within the test cell, unless CO_3^{2-} is added to complex the dissolved U^{6+} .
- the $\text{UO}_3 \cdot x\text{H}_2\text{O}$ layer on the UO_2 surface tends to be cracked, porous, and unprotective.

More complete progress reports on this work are available.(2,3)

Hydrothermal Reactions of UO_2 - P. Taylor

Hydrothermal reactions of UO_2 pellets at 250°C in air-saturated water have shown $\text{UO}_3 \cdot 0.0.8\text{H}_2\text{O}$ to be a primary product. Large, well-formed crystals of this yellow U^{6+} phase were observed on the pellet surface.

LEACHING OF SIMULATED HIGH-LEVEL WASTE BOROSILICATE GLASSES

We presented a brief summary of the development of borosilicate and aluminosilicate glasses for CANDU fuel high-level waste recently.⁽⁴⁾ The purpose of this section is to elaborate upon research on surface alteration layers developed at glass-water interfaces as a result of glass leaching or hydrothermal reactions.

One sodium borosilicate and one sodium-zinc-borosilicate glass simulated-waste glass composition has been selected for detailed study using depth-profiling techniques. The addition of up to 10 weight percent of ZnO has been found to improve glass product chemical durability in modified ISO leach rate tests at 100°C , and a comparison with that of the three-component frit system was required. The two reference glasses had these nominal compositions (weight percent).

6.8 Waste - 10.0 Na_2O - 18.4 B_2O_3 - 64.7 SiO_2

6.8 Waste - 10.0 Na_2O - 10.0 ZnO - 16.2 B_2O_3 - 56.9 SiO_2

Depth-profiling of surfaces of glass samples leached for up to 60 days at 100°C has been accomplished by combining argon ion-beam milling of samples with either electron spectroscopy (ESCA, XPS) or secondary ion mass spectrometry (SIMS). The latter technique development has been a cooperative effort between N. S. McIntyre of WNRE and B. Phillips of Physical Electronics Minneapolis. The results of SIMS experiments are summarized in the next section.

SIMS Analysis of Leached Glass Surfaces - N. S. McIntyre

Preliminary studies have shown that this technique can yield at least a qualitative measure of the change of composition of altered glass layers as a

function of depth normal to a leached surface. This information is important to supplement that obtained by analysis of, say, hydrothermal reaction products generated under simulated thermal-period repository conditions, and to provide some additional guidance as to the nature of alteration-layer chemistry. These observations have been made:

- Sample preparation significantly alters elemental depth profiles and may affect short-term, low temperature leach rates. Specifically, metallographic polishing of borosilicate glasses depletes the surface in Na to a depth of about 60 nm. In contrast, cleaved surfaces show no such variation in composition.
- Leaching of either reference borosilicate glass at 25°C resulted in depletion of both Na and B to a depth of about 200 nm in 1000 hours. These glasses were not detectably phase-separated.
- Low temperature leaching using the recommended ISO leachate-change schedule does not result in excessive concentration of waste-cations at the glass-water interface.
- In contrast, prolonged leaching at 100°C, where leach rates based on sodium loss were greater than 10^{-4} g/(cm²·day), resulted in concentration of several multi-valent cations at the interface. It is not yet clear if this represents a steady-state balance between enrichment (by adsorption or deposition mechanism) and dissolution.
- The change with time of depletion or concentration effects involving Th in particular suggests there may be a correlation of depth profile compositions with the sampling interval specified by the standard leach tests.

Several examples of SIMS analyses (as mass spectrum peak height for the specified mass vs. argon ion-beam sputtering time) are shown in Exhibits 11-17. Additional development of this analytical technique is required before confidence can be obtained in quantitative interpretation of the data.

These conclusions are noteworthy:

- Durable glass samples which are leached for prolonged periods in standard tests behave in unexpected ways, particularly with respect to deposition of multi-valent cations at the glass alteration layer-solution interface.
- the standard leach tests normally used to provide comparisons of glass product durabilities may yield leach rate values which are conservative and high with respect to those within an actual repository environment.
- Depth profile studies indicate that addition of certain cations to waste glasses (i.e., those found to concentrate at the aqueous-glass interface and which promote mineralization of the alteration layer) may lead to in-situ generation of an additional barrier to radionuclide loss.

REFERENCES

1. Cameron, D. J., and G. G. Strathdee. 1979. "Materials Aspects of Waste Disposal in Canada." Proc. Symp. Applications of Ceramics in Nuclear Waste Management. Am. Ceram. Soc. Cincinnati, USDOE. Paper 2-SI-79.
2. Progress Report. Chemistry and Materials Science Division, WNRE PR-WCM-40. 78.10.01 to 78.12.31.
3. Progress Report. Chemistry and Materials Science Division, WNRE PR-WCM-41. 79.01.01 to 79.03.31.
4. Strathdee, G. G., N. S. McIntyre, and P. Taylor. 1979. "Development of Borosilicate and Aluminosilicate Glasses for CANDU Waste." Proc. Symp. Applications of Ceramics in Nuclear Waste Management. Am. Ceram. Soc. Cincinnati, USDOE. Paper 51-SI-79.

EXHIBIT 1. Repository Conditions for Disposal of Spent Fuel

- Container surface temperature, maximum, °C 150
- Volume-average repository temperature, maximum, °C 100
- Groundwater composition
 - Maximum Cl, % 20
 - { Cations Ca^{2+} , Mg^{2+} , Na^{+} ,
 - Anions SO_4^{2-}
 - Pre-flooded, buffered, E_H - conditioned
- Thermal period duration, years 5×10^4
 - Maxima: T_1 40
 - T_2 10^4
- Hydraulic pressure, PSI 1400
- Container Materials:
 - Ticode 12
 - Titanium - Grade 2
 - Inconel 625
 - Stainless steel 316 L
 - Al_2O_3

EXHIBIT 2. Granite if Vault: Room Backfill Temperature Rise as a Function of Time and Without Cooling

EXHIBIT 3. Fuel Leaching

EXHIBIT 4. Fuel Leaching

EXHIBIT 5. Fuel Leaching

EXHIBIT 7. Comparison of Dissolution Rates/Grandstaff

grams $\text{UO}_2 \text{ cm}^{-2} \text{ day}^{-1} \times 10^5$

UO_2 fuel <0.6

Uranite Source

Mitchel County N.C. 2.3

" " " 0.5

Norway 0.15

Rio Algom/Nordic mine 0.02

Wilberforce Canada 0.0066

Vaal Reef 0.06

Rate $\propto$ Purity

EXHIBIT 8. Fuel Leaching

EXHIBIT 9. Current Transients Recorded for $0.5 \text{ mol.dm}^{-3} \text{ Na}_2\text{SO}_4$ at Constant Potential (E) and Different pH Values;
- - - E = -100 mV. (v.SCE); _____ E = +350 mV.

EXHIBIT 10. Cathodic Voltammograms Recorded After 58 Minutes of Oxidation at a Potential of +350 mV (V.SCE) in 0.5 mol. dm^{-3} ; Sweep Rate = 40 $\text{mV}\cdot\text{s}^{-1}$; (1) pH = 10.0; (2) 6.5; (3) 3.8

EXHIBIT 11. Effect of Surface Polishing - SIMS Study

EXHIBIT 12. SIMS Analysis Depletion of Na, B

EXHIBIT 13. SIMS Analysis Depletion of Na, B

EXHIBIT 14. SIMS Analysis Low-Temperature Leaching

EXHIBIT 15. SIMS Analysis Leaching at 100°C

EXHIBIT 16. SIMS Analysis

EXHIBIT 17. Sims Analysis

ELEMENTAL DEPTH COMPOSITION PROFILES FOR 2 WASTE GLASSES FOLLOWING LEACHING

WIPP WASTE CHARACTERIZATION AND EXPERIMENTAL PROGRAMS

by

M. A. Molecke

The Waste Isolation Pilot Plant (WIPP) is intended to serve as a nuclear waste repository for those defense transuranic wastes, both contact-handled and remote-handled, which the Department of Energy (DOE) may designate as requiring deep geologic disposal. The WIPP will also provide a separate underground facility in which in-situ experiments with various waste forms, including high-level waste (HLW) and spent fuel, may be conducted.

The DOE has also recommended (but not determined) that the WIPP be used to demonstrate the disposal of a limited number (no more than 1,000) of spent fuel assemblies from commercial nuclear reactors.

All the wastes, both TRU and spent fuel, placed into the WIPP for intended disposal would be retrievable for the periods required to demonstrate the validity of the disposal concept. These periods are not expected to exceed 10 years for TRU waste and 25 years for spent fuel. Wastes used in the experimental program will be removed at the conclusion of the experiments.

OBJECTIVES

General

1. Identify issues which have potential impact on the acceptability of Southeast New Mexico (SENM) salt for waste isolation.
2. Develop or utilize analytical models to characterize the phenomena associated with each issue.
3. Establish data base for application of models.
4. Perform experiments to assess the validity of models and assumptions.
5. Perform demonstration tests to establish credibility of supporting technology.

6. Provide supporting data for design, safety assessment, and environmental impact.

Specific

1. To generate and evaluate data in support of the development of trans-uranic waste acceptance criteria for WIPP.
2. To quantify interactions of high-level waste forms in SENM bedded salt environments to support safety assessment studies and the definition of the experimental area in the WIPP facility.
3. To obtain data and commensurate constitutive models which describe the response of rock salt formation to loads imposed during excavation and upon emplacement of heat producing wastes. The information will support the Title I design, preliminary safety analysis report, Title II design, and the final safety analysis report.
4. To provide data on the migration of radionuclides in WIPP strata for inclusion in consequence analysis studies.
5. To assess the permeability of SENM rock salt in support of the waste acceptance criteria (WAC) and the criteria for sealing of penetrations.
6. To analyze the migration of brine inclusion in the presence of heat sources for development of conditions for waste/container/salt interaction.
7. To develop a technological base for determining the feasibility of plugging boreholes and other penetrations in support of facility decommissioning and commensurate safety analyses.
8. To perform demonstrations and experiments which allow assessment of design assumptions and operating procedures.
9. To develop instrumentation not commercially available; to support laboratory, bench scale, and in-situ experiments.

Data and interpretation are needed to provide the basis for a decision on acceptability of waste forms for the WIPP. Concerns such as gas generation,

migration enhancement, and combustibility may require alteration of TRU waste forms or containers. These issues and their potential impacts must be assessed to support decisions to process waste or incorporate compensating factors into the design.

The safety assessment program requires source term information on the interaction of heat producing wastes and salt. Information on leach rate, canister corrosion, and radiation damage production must be obtained under conditions of temperature, pressure, and brine presence which may be postulated for WIPP. This information will also provide the basis for definition of experiments and retrieval methods for the WIPP experimental facility.

EXHIBIT 1. The WIPP Reference Repository

EXHIBIT 2. Technical Issues for WIPP Research and Development Program

- ◆ Waste interaction
 - a) TRU degradation and gas generation
 - b) HLW and canister degradation
- ◆ Rock response
 - a) Room closure and retrievability
 - b) Canister motion
 - c) Deformation of overlying formations
- ◆ Repository sealing
 - a) Permeability
 - b) Fluid migration
 - c) Borehole and shaft sealing
 - d) Radionuclide migration.
- ◆ Repository design and operation

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	MODELING	LABORATORY	BENCH SCALE	PRE WIPP INSITU	WIPP	
TRU CHARACTERIZATION						} SUBTASK 1
HLW INTERACTIONS						
THERMAL/STRUCTURAL INTERACTION						} SUBTASK 2
NUCLIDE MIGRATION						
PERMEABILITY						} SUBTASK 3
BRINE MIGRATION						
BOREHOLE PLUGGING						} SUBTASK 4
OPERATION & DESIGN SUPPORT						
INSTRUMENTATION DEVELOPMENT						} SUBTASK 5

BENCH SCALE &
INSITU PROGRAM

TASK IV
SUBTASK 1

EXHIBIT 4. WIPP TRU and HLW Characterization and
Interaction Programs: Objectives

- Quantify concerns of behavior, degradation, interactions (leaching, migration, gas generation)
- Consequence and risk assessment studies
- Technical basis for NRC licensing of WIPP
- Basis for waste acceptance criteria
- Theoretical models for predictive capability
- Accelerated aging experiments, model verification
- Demonstration of acceptable environmental safety

EXHIBIT 5. WIPP Transuranic Waste Characterization Program

Phases

- Laboratory studies
 - a) FY76 - FY79
 - b) FY80
 - c) Existing wastes/developmental forms
- In-situ pre-WIPP dedicated area
 - a) Corrosion demonstration
 - b) Getter development - testing
 - c) Leaching
- WIPP in-situ TRU waste testing boundary conditions, degraded containers.

EXHIBIT 6. WIPP TRU CH Level Temperature

75 KW/ACRE
1500 ACRES
500 FEET BELOW

EXHIBIT 7. Gas Generation from TRU Wastes

- Mechanisms of waste degradation, gas production
 - a) Radiolytic – organic contained water content
 - b) Thermal and catalyzed pyrolytic – organic matrices, waster vapor release
 - c) Chemical corrosion – metals, oxygen, and water rate controlling
 - d) Bacterial – organic matrices: gas production, conversion, consumption
- Primary Gases Produced
H₂, CO₂, CO, CH₄, O₂, H₂O, NO_x, He
- Concerns of Gas Generation
 - a) Long-term: pressurization of repository
breach in containment integrity
 - b) Operational Phase
 - 1. flammable, explosive, toxic concentrations of gases
 - 2. fuel for fire, with initiating event
 - 3. particulate contamination carrier
 - 4. effects on mine design, operation
- Areas of WIPP Study
 - a) kinetics, species, total extent of gas generation
 - b) predictive, analytical modeling of gas generation
 - c) additives, techniques for reducing generation rates
 - d) gas accumulation analysis
 - e) permeability studies on gas dissipation
 - f) mine response to gas accumulation
 - g) WIPP TRU waste acceptance criteria; to limit gas generation

EXHIBIT 8. WIPP Transuranic Waste Characterization Program

DGOT: Radiolytic and thermal degradation of organic TRU wastes - LASL

RTC: Radiolytic degradation and gas generation from concrete matrix TRU wastes - SRL

BDOT: Bacterial degradation of organic TRU wastes - UNM, LASL

CAT: Corrosion studies and anti-corrosion coatings for TRU waste containers - Sandia

CG: Generation of gas from corrosion of TRU waste containers - Sandia

LDW: Leaching of developmental TRU waste matrices - Sandia

COWP: Combustibility testing of TRU waste packages - Sandia

EXHIBIT 9. WIPP Transuranic Waste Characterization Program

Participants:

Martin Molecke - Sandia, Program Manager

Stan Kosiewicz - LASL, CMB-1

Bruce Barraclough - LASL, CMB-1

Ned Bibler - SRL

Doug Caldwell - UNM, Biology

Ben Barnhart - LASL, H-9

Claude Zobell - Scripps

Jeff Braithwaite - Sandia, 5831

John Milloy - Sandia, 4541

EXHIBIT 10. Intercomparison of Measured Gas Generation Rates

<u>Mechanism</u>	<u>Material</u>	<u>Total Gas Rate (moles/yr drum)</u>	<u>Comments</u>
Radiolytic	Cellulosics	0.13 ± 0.03	LASL, SRL
	PVC	0.47	LASL
	HAC concrete/ash	0.04-0.002	SRL
Thermal	Cellulosics	(0.2-2)	40°, calc.
	Cellulosics	15-20	70°, LASL
	Composite	(0.2-2)	40°, calc.
	Composite	7-13	70°, LASL
	Polyethylene	(0.2-2)	40°, calc.
	Polyethylene	18	70°, LASL
Bacterial	Composite	2.6-3.6	25°, UNM
	Composite	22-5.0	40°, UNM
	Composite	36-94	50°, UNM
		(aerobic-anaerobic)	
Corrosion	Mild steel	2.0	deaerated brine inundation, SLA
Alpha decay	He generation	1.5 x 10 ⁻⁶	

EXHIBIT 11. WIPP Transuranic Waste Characterization Program
Related Studies

- Salt bed permeability to gases – Sandia
 - TRU waste gas generation accumulation analysis – Sandia
 - Mine response to gas pressurization – Sandia
 - Criticality concerns for TRU wastes – UNM, Biology, Geology; LASL
 - Radionuclide migration studies – Sandia, ANL
 - Getter development program – Sandia
- A. Rocky Flats Plant, lead lab for TRU waste form immobilization
- B. Battelle PNL, WISAP program, waste form development

EXHIBIT 12. WIPP Microbial-Waste Interaction Study
(UNM-Biology and LASL H-9); BDOT

- Microflora enumeration
 - a) LASL TRU site soil, composite waste TRU containers, WIPP cores and environments
 - b) Determine colony population density; bacterial, fungi identification by genus.
- Methylation of lanthanides, actinides
 - Volatilization, increased retention/toxicity
 - Eu Th Pu --Methylcobalamine
- Microbial chelation and degradation
 - a) Mobility enhancement
 - b) Reconcentration mechanism
 - c) Citrate, EDTA, C-14 labeled
- Microbial modification-actinide oxidation states
 - Mobility enhancement
- Gas generation - microbial degradation
 - Production, consumption, transformation
- Application to shallow land burial

EXHIBIT 13. Environmental Conditions for TRU Waste Container Corrosion Demonstration (Pre-WIPP dedicated area)

EXHIBIT 14. WIPP Transuranic Waste Characterization Program
In-Situ WIPP Tests

- **Emplacement variables:**
 - a) normal operation procedure
 - b) credible boundary conditions, degraded
 - c) temperature: 25°, 40°, 70°
 - d) with/without: brine, getter
- **Monitoring/sampling:**
 - a) gas concentrations
 - b) engineering, emplacement operations
 - c) corrosion, radionuclide migration
- **Emplacement test conditions: (Groups of 9)**
 - a) nondegraded, 25°, salt backfill
 - b) nondegraded, 40°, salt backfill
 - c) nondegraded, 70°, salt and getter backfill
 - d) degraded, 25°, salt backfill
 - e) degraded, 70°, salt and getter backfill
 - f) degraded, wetted, 25°, salt and getter backfill
 - g) degraded, wetted, 40°, salt and getter backfill
 - h) degraded, wetted, 70°, salt and getter backfill

EXHIBIT 15. WIPP HLW Experimental Studies

- HLW brine leaching
- Waste-salt interactions (dry, moist)
- Metallurgy-corrosion testing
- Overpacks, anti-corrosion coatings
- Stored energy study
- Getter development study
- Radionuclide mobility, sorption, modeling
- In-situ experiments, demonstrations
- (Brine migration testing)

EXHIBIT 16. WIPP HLW Experimental Program Phases

- Laboratory studies
- Gamma irradiation facility, Sandia
- WIPP/WISAP interactions – PNL
- Pre-WIPP dedicated area
 - a) leaching, interactions
 - b) corrosion
 - c) getter development
- WIPP in-situ experiments

EXHIBIT 17. WIPP HLW Experimental Program

HLWL: High-level waste leaching
Jeff Braithwaite, Sandia

HLWSI: High-level waste salt interactions
Jeff Braithwaite, Sandia

HLWM: 1. High-level waste canister/overpack metallurgy
Jeff Braithwaite, Sandia

2. Slow strain rate stress corrosion cracking
Nick Magnani, J. Munford, Sandia

WSES: WIPP stored energy study
George Arnold, Sandia

Program Manager – Martin Molecke, Sandia (4512)

EXHIBIT 18. WIPP HLW Experimental Study
HLW Brine Leaching Sandia-5831

1. Experimentally evaluate effects of variables on leach rate; realistic conditions; developmental HLW forms
 2. Determine radiolysis products, radiation damage effects on leach rate; specific cation leaching
 3. Microstructural exam of leached samples
 4. Develop and verify intrinsic leach rate model
 5. Prepare, perform pre-WIPP in-situ leach tests
- Interface: BPNL, SRL, Sandia (Safety assessment, migration modeling, migration sorption, TRU leaching, metallurgy), ONWI

EXHIBIT 19. WIPP HLW Experimental Study
Waste-Salt Interactions (Dry, Moist) Sandia-5831

1. Evaluate hot dry salt interactions with waste form and canister materials, compare to HLW leaching, corrosion
 2. Evaluate moist salt-waste-canister interactions, microstructural phase examination
 3. Determine HLW-salt interactions, effects on leaching sensitization
- Interfaces: SRL; ONWI; Sandia (HLW leaching, corrosion, safety assessment); PSAR

	FY78	79	80	81
			• PSAR	
1.		Φ_1	Φ_2	
2.		Φ_1	Φ_2	
3.				

EXHIBIT 20. WIPP HLW Experimental Study
Metallurgy-Corrosion Testing Sandia-5831

1. Determine brine corrosion rates, candidate materials, representative conditions, as function of multivariables
 2. Accelerated electrochemical corrosion tests
 3. Evaluate slow strain rate stress corrosion cracking
 4. Evaluate radiolysis effects on brine-metal system
 5. Perform pre-WIPP in-situ corrosion tests
 6. Define, verify corrosion reaction rate model
- Interfaces: SRL, ONWI, Westinghouse, Seabed and Elleana and Conasauga programs, Sandia - leaching, interaction, safety assessment, engineering

EXHIBIT 21. WIPP HLW Experimental Study
Stored Energy in WIPP Rocksalt Sandia-5112

1. Program low dosage irradiations, calorimetry measurements
 2. Perform high-dosage irradiations, evaluate effects of impurities
 3. Study radiation damage effects on materials strength
 4. Define, verify kinetics of stored energy release from WIPP rocksalt
- Interface: ORNL, Brookhaven, safety assessment

	FY78	79	80	81
1.	 Φ_1		Φ_2	
2.		Φ_1	Φ_2	
3.		Φ_1	Φ_2	
4.		Φ_1	Φ_2	

EXHIBIT 22. Radionuclide Migration

- Static sorption in brine/groundwater solutions
- Flow through kinetic measurements
- Identification of complexing agents
- Artificially emplaced barriers
- Reconcentration of fissile species

EXHIBIT 23. Related Program Areas

- TRU characterization
- HLW characterization
- Brine migration

EXHIBIT 24. Radionuclide Migration-Getter Development
(Sandia - Nowak, 5812)

- Screening studies: Candidate materials
 - a) Clays: Hectorite, Montmorillonite, Kaolin
 - b) Soils: Dewey Lake redbed, Caliche, Tuff
 - c) Zeolite: Zeolon
 - d) Tracer: Brine A and B, function (pH)
- Mechanisms for radionuclide retardation:
 - a) Precipitation and physical sorption
 - b) Ion exchange and chemical sorption
 - c) Flow barrier
- Empirical and mechanistic studies
- Techniques:
 - a) Batch Kd
 - b) Column flow, bench scale
 - c) Develop defined physical form.

EXHIBIT 25. WIPP Radionuclide Migration
and Associated Chemistry Studies - I

WIPP Site Selection/TRU/HLW Programs
Sandia-5824, ANL, UNM-Chemistry

- Interfaces: Sandia (getter development, leaching, safety assessment, radionuclide migration modeling), UNM-Biology, ONWI/BPNL-WISAP, WACSC
- 1. Measure RN sorption/desorption, kinetics, batch Kd
- 2. RN flow-through measurements, rock and rocksalt cores, and in presence of thermal gradient
- 3. Parameterization of RN sorption, as a function of environmental variables

EXHIBIT 26. WIPP Radionuclide Migration
and Associated Chemistry Studies - II

- 4. Determination of RN oxidation states, chemical species, in realistic WIPP Environment
- 5. Identification of mineralogy controlled sorptive sites in SENM rock
- 6. Evaluate migration enhancement potential of organic and inorganic chelates

EXHIBIT 27. Brine Migration Activities

- Distribution and analyses of fluid inclusions in SENM salt/(evaporites) (USGS)
- Microscopic study of motion of fluid inclusions in salt/evaporites (SLA)
- Study of motion of water in salt under the influence of a heat fluid in a large block of salt; salt blocks II (V-1) (SLA)
- Study of water release phenomena which occurs when heating of salt stops (RE/SPEC)
- Study effect of temperature gradient on brine migration (RE/SPEC)
- Temperature induced gas release in salt (other than and including water) (SLA)
- In-situ activities – see thermostructural (heater) experiments
- Interfaces
 - a) external: ONWI, USGS, FRG, ORNL
 - b) internal: HLW, thermostructural, nuclide migration, operations and design

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