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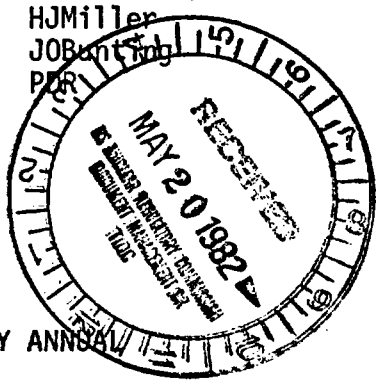
MEMORANDUM FOR: Michael J. Bell, Chief
High-Level Waste Licensing
Management Branch
Division of Waste Management

FROM: F. Robert Cook
High-Level Waste Licensing
Management Branch
Division of Waste Management



SUBJECT: MATERIALS RESEARCH SOCIETY; RESEARCH SOCIETY ANNUAL MEETING; REPORT OF -

The following summarizes significant actions, observations and conclusions associated with my travel to the Materials Research Society Meeting in Boston, Mass. on November 17 and 18, 1981.

A. I presented my prepared speech on Waste Management, High-Level Licensing activities with emphasis on waste package work. This paper is attached.

B. Some 50 odd papers were given at the meeting. Abstracts of these papers are attached. The full text of each paper will be published late in 1982.

C. I met and talked with a dozen or more people attending the meeting. Of particular interest was an A. D. Little representative, Aviva Brecher, who is involved in preparing a model for DOE for evaluation of engineered system/waste package performance.

The work stems from modeling originally done by SAI for DOE. This SAI code is called BARIER. A. D. Little in conjunction with Geotran is refining the BARIER model and preparing SPECTER.

D. Papers of particular interest are the following relative to waste package performance.

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1. C-4 - Corrosion of Structural Materials in Clay Environments (copy on file in Material Section)

2. C-7 - Sandia HLW Package Interaction Test

The first paper identifies 90 year old data for iron structures.

The second paper given by M. A. Molecke highlighted SNL approach to provide performance verification via test, vice predictive models, in contrast to the approach being taken to handle waste form degradation.

ORIGINAL SIGNED BY

F. Robert Cook
High-Level Waste Licensing
Management Branch
Division of Waste Management

Enclosures:
As stated

DIST: TICKET NO:

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NUCLEAR REGULATORY COMMISSION ACTIVITIES RELATED TO HIGH-LEVEL WASTE MATERIALS ISSUES*

F. ROBERT COOK
Nuclear Regulatory Commission, Division of Waste Management, High-Level Waste Licensing Management Branch, Washington, D. C., 20555

ABSTRACT

This paper describes the materials related activities of the Nuclear Regulatory Commission's (NRC's) staff in the area of high-level waste licensing of a geologic repository for nuclear waste. It frames these activities in the context of existing draft regulations for high-level waste disposal.

INTRODUCTION

The activities of NRC's High-Level Waste Licensing Management Branch in the Division of Waste Management relate to anticipated licensing of deep geologic repositories for waste. These activities fall into four categories which are summarized below:

High-Level Waste Management Materials Section Activities

(a) Gaining understanding, building a technical consensus and advising DOE (current)

(b) Site characterization report evaluation (1982-1983)

(c) West Valley Project waste form/canister report evaluation (1984)

(d) License application assessment (1987-1989).

This paper focuses on the Staff's activities related to performance of the waste package and the engineered system materials issues, since this reflects the author's own area of cognizance. The paper addresses the definition of the waste package and other related terms later in discussion of NRC's proposed performance objectives.

As indicated by the dates, the activities listed are roughly in chronological order. Most of the staff's current effort is related to Item A - building a technical consensus as to how to reliably predict waste package and engineered system performance and otherwise advising the Department of Energy (DOE) of the Staff's technical concerns and needs for information to accomplish licensing.

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* This paper is derived from a speech presented to the MRS on November 17, 1981, by the author.

BACKGROUND

The paper will discuss these activities in some detail, but first, in order to put the Staff's activities into their proper context, it will review key features of NRC's proposed rule concerning the waste package and the engineered system. The Staff has proposed to establish minimum requirements for each of the major barriers of a repository identified below:

Major Barriers

(a) Natural geologic environment

(b) Engineered system
  (1) Underground Facility
  (2) Waste packages.

This reflects the consideration that meeting minimun design goals or performance objectives will substantially enhance the Commission's confidence that the final EPA standards will be met. In addition, it is generally considered by the technical community that a multiple barrier system is necessary to obtain reasonable assurance of long-term waste isolation in view of uncertainties that attach to reliance on performance of a geologic setting alone. This premise also has been endorsed by the Government's Inter-agency Review Group (IRG).

The following definitions provide clarification of several key terms utilized in the Commission's proposed rule.

Definitions in 10 CFR 60 (Proposed)

Anticipated Processes and Events - Means those natural processes and events that are reasonable likely to occur during the period the intended performance objective must be achieved and from which the design bases for the engineered system are derived.

Containment - Means the confinement of radioactive waste within a designated boundary.

Engineered System - Means the waste packages and the underground facility.

Overpack - Means any buffer material, receptacle, wrapper, box or other structure, that is both within and an integral part of a waste package. It encloses and protects the waste form so as to meet the performance objectives.

Underground Facility - Means the underground structure, including openings and backfill materials, but excluding shafts, boreholes, and their seals.

Waste Form - Means the radioactive waste materials and any encapsulating or stabilizing materials, exclusive of containers.

Waste Package - Means the airtight, watertight, sealed container which includes the waste form and any ancillary enclosures, including shielding, discrete backfill and overpacks.

The proposed rule contains three performance objectives which will affect the design of the waste packages and the engineered system in a major way and relate to materials issues. These are stated below:

Retrievability. The geologic repository operations area shall be designed so that the entire inventory of waste could be retrieved on a reasonable schedule, starting at any time up to 50 years after waste emplacement operations are complete. A reasonable schedule for retrieval is one that requires no longer than about the same overall period of time than was devoted

to the construction of the geologic repository operations area and the emplacement of wastes.

Containment. The engineered system shall be designed so that even if full or partial saturation of the underground facility were to occur, and assuming anticipated processes and events, the waste packages will contain all radionuclides for at least the first 1,000 years after permanent closure. This requirement does not apply to TRU waste unless TRU waste is emplaced close enough to HLW that the TRU release rate can be significantly affected by the heat generated by the HLW.

Control of Releases. For HLW, the engineered system shall be designed so that, after the first 1,000 years following permanent closure, the annual release rate of any radionuclide from the engineered system into the geologic setting, assuming anticipated processes and events, is at most one part in 100,000 of the maximum amount of that radionuclide calculated to be present in the underground facility (assuming no release from the underground facility) at any time after 1,000 years following permanent closure. This requirement does not apply to radionuclides whose contribution is less than 0.1% of the total annual curie release as prescribed by this paragraph.

Retrievability

The first performance objective relates to retrievability of waste. The major consideration involved in providing retrievability will be deciding how to cope with heat generated by the waste and retained by the host rock up to 50 years after emplacement operations are complete. Excessive repository temeperatures could make cooling of tunnels necessary in order to provide practical worker access. Thus, the insulating characteristics of bulk materials used to backfill the repository, heat generation rates of waste packages, their emplacement density in the repository and the heat dissapating properties of the environment will interact to create the repository's thermal conditions after emplacement.

The waste package and engineered system designers have considerable flexibility in selecting design parameters to mitigate the problems associated with retrievability. Of particular interest is the heat generation rate of the package. Since over 90% of the heat in young commercial high-level waste originates from the isotopes of cesium and strontium, in the case of reprocessed waste, it appears prudent to consider handling these isotopes separately from the rest of the long-lived isotopes. Special provisions for allowing these isotopes to decay while the bulk of the waste is being emplaced in the repository would then be possible. (Parenthetically, long-term storage of spent fuel before emplacement would serve a similar prupose of reducing heat input to a repository.) It should be noted that the separate handling of cesium and strontiun offers other potential advantages in reducing the surface temperature of the majority of the waste packages and providing the options of increased package size as well as allowing increased placement densitities in the repositories. The latter option appears cost effective in that it would allow a smaller repository for a given inventory of high-level waste.

While this objective of retrievability obviously requires considerable designer attention, it does not present the problem associated with gaining reasonable assurance of compliance during licensing proceedings that other performance objectives for containment and release over the long term do. This conclusion reflects the Staff perception of the current acceptability of analytic procedures requried to assess issues associated with retrievability such as the heat transfer problem just discussed. This point is emphasized since it reflects the reason behind the Staff's focus on generating a technical consensus for predicting long-term performance of the engineered

systems and its waste packages to handle this unique engineering/design problem.

Containment

The proposed performance objective which is generally considered to be hardest to prove is that of 1,000 year containment. However, the Commission stated in Section 10 CFR 60.101 relative to the standard for proof in the proposed rule, "In particular, Section 60.41(c) requires a finding that the issuance of a license will not constitute an unreasonable risk.

"While these performance objectives and criteria are generally stated in unqualified terms, it is not expected that complete assurance that they will be met can be presented. A reasonable assurance on the basis of the record before the Commission, that the objectives and criteria will be met, is the general standard that is required. For Section 60.111 and other portions of this sub-part that impose objectives and criteria for repository performance over long times into the future, there will inevitably be greater uncertainties. Proof of the future performance of engineered systems and geologic media over time periods of a thousand or many thousands of years is not to be had in the ordinary sense of the word. For such long-term objectives and criteria, what is required is reasonable assurance making allowance for the time period and hazards involved, that the outcome will be in conformance with those objectives and criteria."

With this position the Staff considers the Commission has provided for accepting less than 100% reliability in the waste packages and the engineered system's performance. This also suggests that reliability assessment of long-term waste package and engineered system performance is warranted to systematically evaluate and quantify the degree of assurance of performance the design will provide.

It is emphasized that the key features of this performance objectives are: (1) Only anticipated processes and events need be considered. (2) The entire engineered system is to be designed such that a component of this system, the waste package, will perform satisfactorily. This suggests that an expected function of the engineered system will be to create a desirable environment for the waste packages. (3) The waste package represents a unique barrier in the multiple barrier system discussed heretofore, and, with the 1,000 year requirement is redundant with the geologic setting which is requred to have ground water travel times to the accessible environment of at least 1,000 years. These two barriers assure isolation of short-lived fission products in high-level waste.

Control of Releases

The third major performance objective for the engineered system is that of controlled release. Key features of this performance objective are: (1) The entire engineered system can be utilized to achieve the specified release rate of one part in 100,000; (2) The releases allowed are radionuclide specific; (3) The base inventory used to calculate allowable releases is the maximum which exists after 1,000 years following repository closure; and (4) Only the most prevalent isotopes are to be considered.

It should be noted that there are no performance objectives specified for waste forms. This allows the designer to utilize other components in the engineered system to help produce the desired controlled release.

STAFF ACTIVITIES

With this background, it is now appropriate to describe the Staff's current activities which are aimed at (1) understanding waste packages and the engineered system's long-term performance, and (2) communicating this understanding to DOE, their contractors, and the technical community. These are summarized below:

Waste Management High-Level Branch Actions to Understand Waste Package Performance

(a) Reviewing high-level waste technology

(b) Independent technical assistance from contractors

(c) Independent research

(d) Organization of information needs (schedule/overview documents)

Item (a) -- *Reviewing High-Level Waste Technology* -- is accomplished by the Staff thorugh review and evaluation of DOE waste management reports and reports from other sources in the technical community. The Staff has also contracted with the Brookhaven National Laboratory (BNL) to provide independent technical assistance, item (b), in this review and evaluation activity. Brookhaven has written several reports during the past year. NRC is currently preparing to print and distribute these reports to the technical community.

Independent research, item (c), is currently being accomplished by both BNL and Argonne National Laboratory (ANL) under the direction of the NRC Office of Research. At BNL the work is focused on identifying failure mechanisms in candidate waste package container materials. Current emphasis is on Ticode-12 alloy. Brookhaven is scheduled to issue quarterly reports on this research. The research effort at ANL is intended to investigate engineered system performance. The investigation makes use of a high-temperature, high-pressure system in which interactions between waste forms, other waste package materials, backfill materials and ground water can be determined. A key feature of the ANL testing is the use of aged materials in selected runs to help assess long-term performance.

Item (d) above refers to preparation of an internal management tool. This overview/schedule document will help the Staff set priorities for research and additional technical reviews. It will eventually identify all information the Staff will need to accomplish licensing and other related duties. It will identify the schedule for acquiring specific information as well as sources. It will serve a purpose analogous to that which a "PERT" chart serves in the development and production of complex equipment, i.e., that of identifying milestones in the critical path of our information gathering needed to accomplish licensing. Although this document is still evolving, the Staff intends that its format be such as to organize information in a logical manner which allows the reviewer to ascertain by inspection why particular information is needed. Since evaluation of waste package and engineered systems performance is at the heart of the licensing activity, the Staff expects this format will reflect a waste package failure mode analysis or system degredation model or other analytic technique which the Staff considers acceptable for purposes of licensing.

The following are the Staff Techical Positions which it is preparing as vehicles to identify information needs to DOE.

Staff Technical Positions

(a) Waste Package Performance After Repository Closure

(b) Reliability Assessment.

The first document, Waste Package Performance After Repository Closure, is being drafted by BNL. This document will focus most of the Staff's efforts since it will present a description of the evaluation the Staff considers necessary for waste packages. Where pertinent parts of this evaluation exist within the technical community or have been prepared by DOE or their contractors, the Staff Technical Position will identify such parts. Thus, for example, for structural analyses this Staff Technical Position may invoke the analysis or criteria required by the ASME Code. Where design specific material data are required to accomplish the necessary evaluation this Staff Technical Position will refer to accepted test techniques for obtaining such data. For example, where appropriate ASTM test procedures can be used they will be identified and where Materials Characterization Center test procedures are appropriate they will be identified. Where accepted test procedures do not exist the Staff Technical Positions will identify information which must be presented to qualify test techniques used to determine the desired properties or relationships.

In all cases where models are used to project performance of the waste package, the Staff will strive to invoke those models which will provide reliable predictions of performance relative to 10 CFR 60 performance objectives and this determination of reliability will be based on a consensus of the technical community.

As suggested by discussion of the Staff's overview/schedule document, the organization of this Staff Technical Position will stem from a failure mode analysis or equivalent of the waste package and the engineered system. Results of this analysis will be required to evaluate the designs presented in a repository license application. A key step in specifying such a failure mode analysis is first identifying all potential failure modes of the components to be evaluated. This requires considerable engineering judgment and some design specific inforamtion. The Staff will again strive to reflect a consensus of the technical community as to the failure modes which must be considered for evaluating candidate waste packages and engineered systems.

The second Staff Technical Position is Reliability Assessment. This assessment will again be linked to a waste package failure mode analysis or equivalent. It will necessarily require subjective input data to typify the reliability of predictive models used in the failure mode analysis. It is here that the judgement of the technical community will establish the reliability of selected models.

CONCLUSION

The Staff considers obtaining the consensus of the technical community on open technical issues related to waste management of utmost importance. The Staff considers desirable the actions of the Materials Characterization Center to organize workshops to develop models for waste form degredation. Such models will be a necessary part of the overall evaluation of release of

radionuclides from the engineered system. The Staff considers these workshops provide the arena for building the desired consensus. The Staff considers similar workshops should be organized by DOE for the purpose of developing and qualifying other key models necessary for evaluation of the waste package and engineered system long-term performance. Specifically, based on its activities described heretofore, it considers the following areas need input of the technical community via workshops or other forums linked up to task forces to produce predictive models with sufficient qualifying data to provide bases for determining a reasonable reliability.

Areas Needing Technical Community Consensus

(a) Long-term container degradation models

(b) Reliability analyses

(c) Failure mode analyses for waste packages and the engineered system

(d) Repository environment modeling

SYMPOSIUM D

INTERNATIONAL SYMPOSIUM ON THE SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT

Chairman: Stephen V. Topp,
Du Pont - Savannah River Laboratory, Aiken, SC

November 16-19, 1981

Session A

Monday Morning, 8:15-12:15

Chemical and Physical Properties of Waste Forms - Session I

Presiding: John A. Stone, Du Pont - Savannah River Laboratory and Peter Zuhlke, Federal Republic Germany

8:15 Greeting and Opening Remarks - S.V. Topp

8:30 Invited Keynote Address: "An Experimental Comparison of Alternative Solid Forms for Savannah River High Level Wastes," J.A. Stone, Du Pont - Savannah River Laboratory

9:00 "Factors Affecting the Leach Rates of Perovskite and Sphene," G.M. Bancroft, J. Metson, H.W. Nesbitt, W.S. Fyfe, and P.J. Hayward, Western Ontario University

9:20 "Effects of Processing Parameters on SYNROC Performance," V.K. Sethi, J.K. Bates, and R.M. Arons, Argonne National Laboratory

9:40 "Behavior of Titanate-Based Waste Forms in Aqueous Solutions," R.G. Dosch, Sandia National Laboratories

10:00 B R E A K

10:15 "Iron-Enriched Basalt for Containment of Nuclear Wastes," J.M. Welch, P.V. Kelsey Jr., S.P. Henslee, R.L. Tallman, R.P. Schuman, R.M. Horton, C.W. Sill, D.E. Owen, and J.E. Flinn, EG&G Idaho Inc.

10:35 "Studies of Pollucite," E.R. Vance, B.E. Scheetz, M.W. Barnes, and B.J. Bodnar, The Pennsylvania State University

10:55 "Evaluation of Ceramic Materials to Immobilize ICPP Calcines," B.A. Staples, H.S. Cole, J.C. Mittl, Exxon Nuclear Idaho Company

11:15 "Immobilization of Savannah River High-Level Wastes in SYNROC: Results from Product Performance Tests," J. Campbell, C. Hoenig, C. Bazan, R. Ryerson, and R. Van Konynenburg, Lawrence Livermore National Laboratory

11:35 "The Application of Mössbauer Spectroscopy to the Characterization of Nuclear Waste Forms," L.A. Boatner and M.M. Abraham, Oak Ridge National Laboratory, and P.G. Huray, M.T. Spaar, S.E. Nave, and J.M. Legan, University of Tennessee

11:55 "Photoemission Study of Leached 76-68 Waste Glass Surfaces," D.P. Karim, D.J. Lam, H. Diamond, A.M. Friedman, Argonne National Laboratory, D.G. Coles, F. Bazan, Lawrence Livermore National Laboratory, and G.L. McVay, Battelle Pacific Northwest Laboratory

Session B

Monday Afternoon, 1:30-5:00

Geologic and Geochemical Considerations

Presiding: Kurt Wolfsberg, Los Alamos National Laboratory; Douglas G. Brookins, University of New Mexico; and Eva L.J. Rosinger, AECL, Whiteshell, Canada

1:40 "The Use of ^{222}Rn as a Flow Path Monitor for Studies of Radionuclide Transport in Fissures," J. Hines, D. Cohen, S. Fried, and A.M. Friedman, Argonne National Laboratory

2:00 "Formation and Properties of Americium Colloids in Aqueous Systems," U. Olofsson, B. Allard, K. Andersson, and B. Torstenfelt, Chalmers University of Technology, Göteborg, Sweden

2:20 "Site Characterization for Field Radionuclide Migration Studies in Climax Granite," D. Isherwood, E. Raber, and R. Stone, Lawrence Livermore National Laboratory

2:40 "Nuclide Migration Field Experiments in Tuff, G-Tunnel, Nevada Test Site," B.R. Erdal, R.S. Rundberg, K. Wolfsberg, Los Alamos National Laboratory; D.R. Fortney, K.L. Erickson, Sandia National Laboratories; and A.M. Friedman, S. Fried, and J.J. Hines, Argonne National Laboratory

3:00 B R E A K

3:15 "Predicting Pu Concentrations in Solutions Contacting Geologic Materials," R.G. Strickert and D. Rai, Battelle Pacific Northwest Laboratory

3:35 "Transient Hydraulic Tests in Granite: Fractured Porous Medium Analysis and Results," J.H. Black and J.A. Barker, Harwell Laboratory, UK

3:55 "A Natural Analogue for Storage of Radwaste in Crystalline Rocks," D.G. Brookins, M.S. Abashian, University of New Mexico; L.H. Cohen, University of California-Riverside; and H.A. Wollenberg Jr., Lawrence Berkeley Laboratory

4:15 "Radionuclide Migration: Laboratory Experiments with Isolated Fractures," R.J. Rundberg, S. Maestas, Los Alamos National Laboratory, and J.L. Thompson, Idaho State University

4:35 "Effect of Organic Complexing Agents and Temperature on Adsorption of Radionuclides: Implications for Disposal of Radioactive Waste," A. Maest, S. Tréhu, E. Dillon, and D. Crerar, Princeton University, and J. Means, Battelle Columbus Laboratories

Session C

Tuesday Morning, 8:15-12:00

Canister, Backfill, and Near-Field Interactions

Presiding: John Kircher, Office of Nuclear Waste Isolation, and Takehiko Ishihara, Radioactive Waste Management Center, Japan

8:20 "Diffusion Measurements in Compacted Bentonite," B. Torstenfelt, K. Andersson, B. Allard, and U. Olofsson, Chalmers University of Technology, Göteborg, Sweden

8:40 "Dissolution of Simulated Spent Fuel in Hydrothermal Solutions," W.P. Freeborn, S. Komarneni, B.E. Scheetz, and W.B. White, The Pennsylvania State University

9:00 "Migration Rates of Brine Inclusions in Single Crystals of NaCl," I-Ming Chou, U.S. Geological Survey

9:20 "Corrosion of Structural Materials in Clay Environments," J. Dresselaers, F. Casteels, and H. Tas, SCK/CEN, Mol, Belgium

9:40 "The Dissolution of Irradiated Fuel Under Hydrothermal Conditions," L.H. Johnson, AECL, Whiteshell, Canada

10:00 B R E A K

10:15 "Retardation, Permeability, and Swelling of Candidate Backfill Materials," J.H. Westsik Jr., L.A. Bray, F.N. Hodges, and E.J. Wheelwright, Battelle Pacific Northwest Laboratory

10:35 "PNL-Sandia HLW Package Interactions Test: Phase One," M.A. Molecke, Sandia National Laboratories; D.J. Bradley and J.W. Shade, Battelle Pacific Northwest Laboratory

10:55 "Experimental Studies of Processes Governing the Release and Subsequent Sorption of Nuclides in Granite Repositories," N.A. Chapman, P.J. Dudson, I.J. McKinley, D. Savage, and J.M. West, Institute of Geologic Sciences, Harwell, UK

11:15 "Degradation of Rocks Through Cracking Caused by Differential Thermal Expansion," R.W. Davidge, J.R. McLaren, and I. Titchell, AERE Harwell, UK

11:35 "Development of Engineered Structural Barriers for Nuclear Waste Packages," R.E. Westerman, S.G. Pitman, and R.P. Elmore, Battelle Pacific Northwest Laboratory

Session D

Tuesday Afternoon, 1:20-3:15

Invited Speakers on Overview Topics

Presiding: John D. Tewhey, Jordan Gorrill Associates, and Claude Sombret, Atomic Energy Commission, France

20 "ONWI Overall Program and Scientific Requirements," J. Kircher, Office of Nuclear Waste Isolation

45 "Materials Research for the Canadian Waste Management Program," D.J. Cameron, AECL, Whiteshell, Canada

:10 "History of European Waste Management and Preview of Next Five Years," S. Orlowski, Commission of European Communities

:35 "Material Aspects of NRC High-Level Waste Disposal Regulations," M.J. Bell and F.R. Cook, U.S. Nuclear Regulatory Commission

:55 "Materials Implications of 10 CFR Part 61 (Low-Level Waste)," P.H. Lohaus and R.D. Smith, U.S. Nuclear Regulatory Commission

Session E

Tuesday Afternoon, 3:15-5:00

POSTER SESSION - Geologic, Canister, Backfill Considerations

Presiding: James G. Steger, Los Alamos National Laboratory, and Wayne A. Ross, Battelle Pacific Northwest Laboratory

"A Study of Zirconolite from Sri Lanka and South Africa," R.F. Haaker, R.C. Ewing, University of New Mexico, and T.J. Headley, Sandia National Laboratories

"Clay Minerals in Bedded Salt: Identification, Chemical Composition, and Evidence for Alteration in Brine," L.L. Fasset and D.R. Palmer, University of Texas

"Experimental and Theoretical Analyses of Small-Scale Radionuclide Migration Field Experiments," K.L. Erickson and D.R. Fortney, Sandia National Laboratories

"Reference Laboratory Testing for Backfill," R.M. Chung and F.Y. Yokel, National Bureau of Standards

"Studies of Localized Corrosion at High Temperatures of Pit and Crevice Microenvironments," V.K. Hardman and J. Kruger, National Bureau of Standards

"Strontium-Basalt Reactions Under Nuclear Waste Repository Conditions," S. Komarneni, The Pennsylvania State University

"Backfill-Waste Interactions Under Radwaste Repository Conditions," N. Sasaki, Tokai Works, Japan; S. Komarneni, B.E. Scheetz, and R. Roy, The Pennsylvania State University

"Alpha Decay Self-Damage in Cubic and Monoclinic Zirconolite," F.W. Clinard Jr., C.C. Land, E.D. Peterson, D.L. Rohr, and R.B. Roof, Los Alamos National Laboratory

"Chemical, Physical, and Engineering Characterization of Candidate Backfill Clays and Clay Admixtures for a Nuclear Waste Repository," S.K. Singh, Materials Research Laboratory, Ltd., Canada

"Radiation Induced Sodium Metal Colloid Formation in Natural Rock Salt from Several Geological Localities," J.J. Loman, P.W. Levy, and K.J. Swyler, Brookhaven National Laboratory

"Study of Polyhalite from the WIPP Site, New Mexico," D.G. Brookins, University of New Mexico

"Uranium-Lead Radiometric Age Determinations of Naturally Occurring U(VI) Minerals: Application to Radwaste Storage," D.G. Brookins, University of New Mexico

"Diffusion of Neptunyl(V)- and Pertechnetate Ions in Marine Sediments," F. Schreiner, S. Fried, and A. Friedman, Argonne National Laboratory

"Radiogeological Assessment of Candidate Sites for Nuclear Waste Repositories, Exemplified by Studies of the Stripa Pluton, Sweden," H.A. Wollenberg, S. Flexser, and L. Andersson, Lawrence Berkeley Laboratory

"Novel Experiments for Understanding the Shallow Land Burial of Low-Level Radioactive Wastes," G.L. DePoorter, Los Alamos National Laboratory

"Identification of Possible High Integrity Containers for Nuclear Waste Disposal," J. Williams, Hittman Nuclear and Development Corporation

"Predictions of Radionuclide Migration Rates for a Subseabed Repository," L.H. Brush, Sandia National Laboratories

Session F

Wednesday Morning, 8:15-11:35

Non High-Level Waste Assessments

Presiding: James G. Steger, Los Alamos National Laboratory, and Ron H. Flowers, AERE Harwell, UK

8:20 "Stochastic Analysis of Groundwater Flow and Contaminant Transport in a Fractured Rock System," F.D. Schwartz, A.S.Crowe, University of Alberta, and L.L. Smith, University of British Columbia, Canada

8:40 "Solidification of Radioactive Wastes with Thermosetting Resin," M. Hayashi, Tokyo Electric; K. Kobayashi, Tohoku Electric; O. Okamoto, Chubu Electric; T. Kagawa, Chugoku Electric; K. Wakamatsu, Japan Atomic; H. Irie, Tashiba Corporation; H. Matsuura and Y. Nakayama, NAIG Laboratory, Japan

9:00 "Nuclear Waste Disposal: The Interface Between Performance Assessment and Research," R.B. Lyon, AECL, Whiteshell, Canada

9:20 "Processing of Titanates and Zeolites, and Use of a Cartridge System for 'Reactor' Wastes," S. Forberg, T. Westermark, K. Svardstrom, RIT, Stockholm; and L. Falth, LIT, Lund, Sweden

9:40 "Performance of Asphalt and Clay Liners as a Uranium Mill Tailings Leachate Barrier," J.L. Buelt, V.Q. Hale, and S.M. Barnes, Battelle Pacific Northwest Laboratory

10:00 B R E A K

10:15 "Behavior of Radionuclides in Fused Waste-Disposal-Site Soil Produced by In-Situ Vitrification," C.L. Timmerman and J.L. Buelt, Battelle Pacific Northwest Laboratory

10:35 "A Comparative Assessment of TRU Immobilization Systems," W.A. Ross, C.O. Harvey, R.O. Lokken, R.P. May, F.P. Roberts, C.L. Timmerman, R.L. Treat, and J.H. Westsik Jr., Battelle Pacific Northwest Laboratory

10:55 "Low-Level Waste Disposal Risk Analysis," S.G. Oston, C.M. Koplik, D.A. Ensminger, J.Y. Nalbandian, and M.F. Kaplan, The Analytic Sciences Corporation

11:15 "Leach Studies of Radionuclides from Solidified Wastes with Thermosetting Resin," K. Suzuki and H. Kuribayashi, JGC Corporation; and W. Morimitsu and I. Ono, Industrial Research Institute of Kanagawa, Japan

Session G

Wednesday Afternoon, 1:30-3:00

Processing Complexities at Full Scale

Presiding: Charles M. Brown, Rockwell-Rocky Flats, and Torbjörn Westermark, Royal Institute of Technology, Sweden

1:30 "Processing Tailored Ceramic Nuclear Waste Forms," J. Flintoff, D.R. Clarke, A.B. Harker, P.E.D. Morgan, and C.M. Jantzen, Rockwell Science Center

1:45 "On-Line Measurements of the Volatilization of Ruthenium in a Vitrification Process," R. Odoj, Institute for Chemical Technology, Jülich, FRG

2:00 "Cementitious Radioactive Waste Hosts Formed Under Elevated Temperatures and Pressures (FUETAP Concretes)," L.R. Dole, J.G. Moore, G.C. Rogers, G.A. West, H.E. Devaney, M.T. Morgan, and J.H. Kessler, Oak Ridge National Laboratory

2:15 "Behavior of Radionuclides at Smelting of Non-Combustible Solid Wastes," M. Osaki, S. Yokoi, Daido Steel Company, Ltd.; and M. Miyagawa, Chubu Electric Power Company, Japan

2:30 "Vitrification of High-Level Radioactive Waste in a Small-Scale Joule-Heated Ceramic Melter," G.B. Woolsey, R.E. Eibling, and Lien-Mow Lee, Du Pont - Savannah River Laboratory

2:45 "Metastable Liquid Immiscibility in Nuclear-Waste Glasses," J.E. Engell and G. Roed, Technical University of Denmark

Session H

Wednesday Afternoon, 3:00-5:00

POSTER SESSION - Non-High-Level, Radiation Effects, Processing, and Chemical and Physical Properties

Presiding: Charles M. Brown, Rockwell-Rocky Flats, and Kurt Wolfsberg, Los Alamos National Laboratory

"Mercury Reduction and Removal During High-Level Radioactive Waste Processing and Vitrification," R.E. Eibling and J.R. Fowler, Du Pont - Savannah River Laboratory

"Interim Waste Forms for High-Level Radioactive Wastes: Processing and Properties," G. Bandyopadhyay and S.M. Gehl, Argonne National Laboratory

"Immersion and Leach Tests on Solidified Decontamination Wastes from Dresden Unit 1," R.E. Barletta, J.W. Adams, and R.E. Davis, Brookhaven National Laboratory

"Tailored Ion Exchange Resins for Combined Cesium and Strontium Removal from Soluble Defense High-Level Waste," M.A. Ebra and R.M. Wallace, Du Pont - Savannah River Laboratory

"Biological Intrusion of Low Level Waste Trench Covers," T.E. Hakonson, Los Alamos National Laboratory

"Stability of I and Sr Radiophases in Cement Matrices," M.W. Barnes, B.E. Scheetz, L.D. Wakeley, S.D. Atkinson, and D.M. Roy, The Pennsylvania State University

"The System $SrMoO_4$-$BaMoO_4$-$CaMoO_4$: Compatibility Relations, The Implications for Supercalcine Ceramics," B.E. Scheetz, W.P. Freeborn, J. Pepin, and W.B. White, The Pennsylvania State University

"Iron-Enriched Basalt and Its Application to Three-Mile Island and West Valley Radioactive Waste Disposal," P.V. Kelsey Jr., J.M. Welch, D.E. Owen, and J.E. Flinn, EG&G Idaho Inc.

"Leaching Studies of Na-Bearing Crystalline Phases in Nuclear Waste Forms," E.R. Vance and T. Adl, The Pennsylvania State University

"Immobilization and Leakage of Krypton Encapsulated in Zeolite and Glass," J.E. Tanner, J.A. Del Debbio, A.B. Christensen, and D.A. Knecht, Exxon Nuclear Idaho Company Inc.

"Solubility Effects in Waste Glass/Demineralized Water Systems," H.T. Fullam, Battelle Pacific Northwest Laboratory

"Immobilization of ^{14}C Formed During Reactor Operations," S. Fried, F. Schreiner, D. Cohen, J. Hines, and A.M. Friedman, Argonne National Laboratory

"Lanthanide Orthophosphates as a Matrix for Solidified Radioactive Defense and Reactor Wastes," M. Petek, M.M. Abraham, and L.A. Boatner, Oak Ridge National Laboratory

"Hot-Pressed Barium Sulphate Ceramics for Immobilization of Medium Level Magnox Waste," A. Briggs, D.V.C. Jones, and G.B. Cole, AERE Harwell, UK

"Immobilization of High-Level Nuclear Reactor Wastes in SYNROC: A Current Appraisal," A.E. Ringwood, V.M. Oversby, and S.E. Kesson, Research School of Earth Sciences, Australia

"The Influence of Gamma Irradiation on the Leaching Behavior of Modified SYNROC-B Ceramic Waste Form," A.G. Solomah, North Carolina State University

"Migration of Radionuclide Chains in Subseabed Disposal," A.K. Ray, University of Kentucky, and H.E. Nuttall, University of New Mexico

"Standard Tests for Thermal Stability of Nuclear Waste Forms," W.J. Gray, R.P. May, and W.J. Weber, Battelle Pacific Northwest Laboratory

"Radiation Effects in Radwaste Glasses: A Reappraisal of Alpha-Recoil Aging as Simulated by Ion Implantation," J.D. Dran, Y. Langevin, M. Maurette, and J.C. Petit, Orsay, France

"Rheological Characterization of Cementitious Grouts Used to Dispose of Intermediate-Level Radioactive Waste by Hydrofracturing of Oak Ridge National Laboratory," E.W. McDaniel and J.G. Moore, Oak Ridge National Laboratory

Session I

Thursday Morning, 8:15-12:00

Radiation Effects on Nuclear Waste Forms

Presiding: Clyde J.M. Northrup Jr., Sandia National Laboratories and Lynn A. Boatner, Oak Ridge National Laboratory

8:20 "Enhanced Dissolution of Glass in the Presence of Salts and Radiation Damage," C. Burman and W.A. Lanford, State University of New York at Albany

8:40 "Influence of Glass Composition and Environmental Parameters on the Durability of Alpha-Recoil-Aged Radwaste Glasses," J.C. Dran, M. Maurette, J.C. Petit, and B. Vassent, Orsay, France

9:00 "Valence State Determination and the Effect of Radiation on Leaching of Borosilicate Glass," D.P. Karim, D.J. Lam, K.L. Nash, A.M. Friedman, J.C. Sullivan, and S. Fried, Argonne National Laboratory

9:20 "Ion Implantation Studies of Nuclear Waste Forms," C.J. Northrup, G.W. Arnold, and T.J. Headley, Sandia National Laboratories

9:40 "Effects of Alpha, Gamma, and Alpha-Recoil Radiation on Borosilicate Glass Containing Defense High-Level Nuclear Waste," N.E. Bibler, Du Pont - Savannah River Laboratory

10:00 B R E A K

10:15 "Properties of Alpha Doped Glasses Referring to the Long Term Disposal of Solidified High-Level Radioactive Wastes," N. Jacquet-Francillon and E. Vernaz, CEA, France

10:35 "Study of the Metamict Transformation in Alpha-Quartz Using High-Resolution Lattice Imaging and Convergent Beam Electron Diffraction," M.R. Pascucci, Case Western Reserve University; J.L. Hutchison, Oxford University, UK; S. McKernan, J.A. Eades, Bristol University, UK, and L.W. Hobbs, Massachusetts Institute of Technology

10:55 "Radiation Effects in Nuclear Waste Glasses," D.G. Howitt, J.F. DeNatale, and D.K. McElfresh, University of California - Davis

11:15 "Influence of Irradiation With Gamma-Quanta and Beams of Accelerated Electrons on the Sorption Parameters of Clay Minerals of the Montmorillonite Group," V.I. Spitsyn, V.D. Balukova, M.K. Savushkina, Academy of Sciences, USSR

11:35 "Microstructural Stability of Waste Glasses Under Irradiation," M. Antonini, A. Manara, and S.N. Buckley, AERE, Harwell, England

Session J

Thursday Afternoon, 1:30-3:50

Chemical and Physical Properties of Waste Forms - Session II

Presiding: Wayne A. Ross, Battelle Pacific Northwest Laboratory, and Gerald H. Daly, U.S. Department of Energy

1:30 "Rutherford Backscattering Investigation of the Leaching Characteristics of Borosilicate Glass," L.A. Boatner, H. Naramoto, C.W. White, and B.C. Sales, Oak Ridge National Laboratory

1:50 "Development of Sphene-Based Glass Ceramics Tailored for Canadian Waste Disposal Conditions," P.J. Hayward and E.V. Cecchetto, AECL, Whiteshell, Canada

2:10 "The Development and Testing of SYNROC C as a High-Level Nuclear Waste Form," K.D. Reeve, E.J. Ramm, D.M. Levins, J.L. Woolfrey, and W.J. Buykx, AAEC Research Establishment, Australia

2:30 "The Leaching Behavior of the Swedish KBS Glasses ABS-39 and ABS-41," H.P. Hermansson and H. Christensen, Studsvik Energiteknik, Sweden

2:50 "Comparative Impact Properties of Five Solid Alternative Savannah River Laboratory Defense High-Level Waste Forms," L.J. Jardine, G.T. Reedy, and W.J. Mecham, Argonne National Laboratory

3:10 "A Methodology for Characterizing Brittle Fracture of Solid Waste Forms from Accidental Impacts," W.J. Mecham, L.J. Jardine, and M.J. Steindler, Argonne National Laboratory

3:30 "Alkoxide Derived Amorphous Solids as an Alternate Nuclear Waste Form," J.M. Pope and D.E. Harrison, Westinghouse Research and Development Center

A1 Invited Keynote Address: "An Experimental Comparison of Alternative Solid Forms for Savannah River High Level Wastes," J. A. Stone, Du Pont - Savannah River Laboratory. No abstract available.

A2 FACTORS AFFECTING THE LEACH RATES OF PEROVSKITE AND SPHENE. G.M. Bancroft, J. Metson, H.W. Nesbitt and W.S. Fyfe, Centre for Chemical Physics and Department of Geology, University of Western Ontario, London, Ontario, N6A 5B7 and P.J. Hayward, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, ROE 1LO.

We report leach rates at 90-100°C for natural samples of perovskite, and sphene, and sphene-based glass ceramics under a variety of conditions. The leach rates are very dependent on: the SA/V ratio, the nature of the sample (eg. crystal, grains, or powders), whether continuous or static tests are used, initial pH and ion concentrations, and whether equilibrium is approached during leaching. The leach rates vary by at least a factor of 3 with an order of magnitude change in SA/V ratio, and even larger differences are found between crystals and fine grains. Both perovskite, sphene and other silicate leach rates drop off rapidly with leach time, and this decrease is related to a buildup of TiO_2 on the surface. Under equilibrium conditions (as determined by stability field diagrams at 100°C), the sphene actually gains weight. These equilibrium solution concentrations are realized in many natural waters.

A3 EFFECTS OF PROCESSING PARAMETERS ON SYNROC PERFORMANCE*, V. K. Sethi, J. K. Bates, and R. M. Arons, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

SYNROC, an assemblage of the titanate minerals perovskite ($CaTiO_3$), zirconolite ($CaZrTi_2O_7$), and "Ba-hollandite" ($BaAl_2Ti_6O_{16}$), has the capacity to accept nearly all of the elements present in high-level radioactive wastes into its crystal lattices. It was recognized early in the development of SYNROC that the crystal chemistry and the distribution of waste elements are influenced by the redox conditions under which the assemblage is consolidated. Since most of the fabrication schemes proposed were based on either hot pressing or hot isostatic pressing, ad hoc redox control was attempted using various metal/metal-oxide oxygen fugacity buffers. At Argonne National Laboratory, conventional sintering under controlled oxygen partial pressure (p_{O_2}) conditions is being studied and appears to be a viable and cheaper fabrication process for SYNROC. Sintering in a controlled environment also enables a systematic investigation of the redox effects on the waste form performance over a wide range of p_{O_2} where metal/metal-oxide buffers cannot be used or are not available. SYNROC pellets were fired in various reducing CO/CO_2 environments at different temperatures. Firing in reducing environments promotes sintering, increases the leach resistance, and reduces the Cs volatility losses. The results show that "good" SYNROC can be fabricated by cold pressing or extrusion, followed by sintering at controlled oxygen partial pressures ($10^{-14} < p_{O_2} < 10^{-12}$) for ~2 h at ~1250°C.

*Work supported by the U. S. Department of Energy.

BEHAVIOR OF TITANATE-BASED WASTE FORMS IN AQUEOUS SOLUTIONS,* R. G. Dosch, Sandia National Laboratories,** Albuquerque, New Mexico, 87185.

One of the principle advantages of titanium-based ceramic waste forms, as compared to glasses, is superior resistance to aqueous attack over a wide range of potential repository conditions including temperature, aqueous phase composition, pH, and hydrological conditions. The behavior of titanates, relative to aqueous attack, is directly related to processing conditions used in preparing the waste form. This study evaluated processing parameters including temperature, waste loading, oxygen fugacity, and additives used to promote the formation of specific phases and their effects on the leaching rates of Cs, Mo, Ca, Sr, Ba, U, T, and Gd. Monolithic samples were consecutively leached in deionized water at temperatures of 22°C, 60°C, 90°C, and 150°C. Additional tests were done at 90°C in both acidic (pH 2) and basic (pH 12) solution and in water in the presence of bentonite clay, which is a major component of most proposed backfill compositions. A reference glass, PNL 76-68, was included in all tests to provide a direct comparison between the two waste forms. The most important processing parameter was found to be oxygen fugacity. Variations of up to five orders of magnitude in Cs leach rates were related to this parameter in materials containing 25% waste. In material containing 10% waste, there appeared to be no dependence of Cs release on oxygen fugacity. The pH of the aqueous phase also appears to have a negligible effect on Cs release rates from titanates. Surface analysis of four samples of leached and unleached titanate samples using helium ion backscattering techniques showed evidence of alteration on only one sample. A gradual depletion of Ca to a depth of about 2000 Å was observed along with a less pronounced depletion of U, rare earths, and possibly Mo in the near surface layers.

* This work supported by the U. S. Department of Energy under Contract DE-AC04-DP00789.
** A U. S. Department of Energy facility.

IRON-ENRICHED BASALT FOR CONTAINMENT OF NUCLEAR WASTES. J. M. Welch, P. V. Kelsey, Jr., S. P. Henslee, R. L. Tallman, R. P. Schuman, R. M. Horton, C. W. Sill, D. E. Owen, and J. E. Flinn, EG&G Idaho, Inc., Box 1625, Idaho Falls, ID 83415.

Simulated high-level waste calcines from the Savannah River Plant (SRP) and the Idaho Chemical Processing Plant (CPP) have been incorporated into iron-enriched basalt at the following waste loadings:

SRP - High Fe Calcine - 35 wt.%; SRP - High Al Calcine - 33 wt.%; SRP - Composite - 40 wt.%; CPP Alumina Calcine - 30 wt.%; CPP Zirconia Calcine - 30 wt.%.

Microstructural analysis, leaching, and fracture toughness values are reported for these waste form specimens. Since preparation of the IEB requires relatively high temperatures (1400-1500°C), the potential for cesium loss from high-level waste was investigated. Cesium doping experiments showed low Cs volatility from the IEB melts as well as low Cs leach rates from the solidified waste form.

Defense waste sludge from the Rocky Flats, CO facility, with and without transuranic elements, was incorporated into iron-enriched basalt (IEB) waste form at 50 wt.% loading. The IEB was synthesized by melting sludge and mixtures of sludge and additives at 1773 K, and controlling the cooling cycle to promote crystal nucleation and growth. The crystalline phases observed, via X-ray diffraction analysis and scanning electron microscopy, were augite, spinel, and apatite. The presence of the apatite phase, not normally associated with IEB, is a result of phosphate in the sludge. The apatite phase does not affect the waste form properties of IEB. The bulk leach rate at 263 K in deionized water for the IEB specimens synthesized from sludge was 6×10^{-7} g/cm^2·d. Specific transuranic element leach rates are reported.

A6 STUDIES OF POLLUCITE. E.R. Vance, B.E. Scheetz, M.W. Barnes and B.J. Bodnar, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

Several aspects of pollucite as a radiophase were studied. These aspects were (i) possible range of stoichiometry at high temperatures, (ii) incorporation of cations other than Cs, Al or Si, (iii) compatibility with other phases occurring in tailored-ceramic formulations, (iv) crystallization kinetics and possible sintering aids, (v) radiation damage response, (vi) transmutation stability and (vii) compatibility with cements.

A7 EVALUATION OF CERAMIC MATERIALS TO IMMOBILIZE ICPP CALCINES. B. A. Staples, H. S. Cole, J. C. Mittle, Exxon Nuclear Idaho Company, Inc., P.O. Box 2800, Idaho Falls, Idaho 83402

Aqueous wastes from the reprocessing of nuclear fuels at the Idaho Chemical Processing Plant (ICPP) are solidified by calcination. It has been determined that the radionuclides of cesium and strontium leach readily from the calcine. Regulatory criteria may require that calcine be immobilized further for final disposal. Candidate materials to immobilize ICPP calcines include borosilicate glass, titanates, tailored ceramics, glass-ceramics and matrix encapsulants. These materials have been prepared with simulated ICPP calcine, their leaching properties determined and compared with those of Formula 127 borosilicate glass. With respect to total mass loss by application of the MCC-1 static leach test, the tailored ceramic (1.0×10^{-5}g/cm^2·day) and 127 glass (1.3×10^{-5}g/cm^2·day) are superior to the other materials tested to date. Likewise, through application of MCC-1, 127 glass (3.5×10^{-5}g/cm^2·day) is superior with respect to cesium leachability than the other materials tested to date. Soxhlet tests have been applied to these materials and potential processing steps are being evaluated.

A8 IMMOBILIZATION OF SAVANNAH RIVER HIGH-LEVEL WASTES IN SYNROC: RESULTS FROM PRODUCT PERFORMANCE TESTS. J. Campbell, C. Hoenig, C. Bazan, R. Ryerson, and R. Van Konynenburg, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California, 94550.

Large samples (up to 15cm diameter) of SYNROC D containing simulated Savannah River (SRL) waste sludge have been prepared and performance tested. Waste loadings of 60-70 wt% for the SRL composite sludge have been achieved; this corresponds to a waste concentration (volumetric) loading of approximately 2.4-2.8 g/cm^3. A typical SYNROC D sample has a density of about 4.0 g/cm^3 with less than 0.2% porosity. The compressive and flexural strengths of SYNROC D are 18,800 and 51,200 psi, respectively and Young's Modulus is 20.15×10^6 psi by ultrasonic measurement. The quantity of respirable fines (less than 10 µm) generated during a constant energy density impact (10J/cm^3) was less than 0.16 wt%. Values for the thermal conductivity (22°C) and the thermal expansion coefficient (22-950°C) were measured to be 1.7 W/m·K and 11×10^{-6} K^{-1}, respectively. Intercomparison of results from static (MCC-1, 2, and 3) and dynamic (MCC-4-type, modified IAEA) leach tests on SYNROC D in deionized water (75 and 90°C) show excellent agreement between the various tests. Normalized leach rates determined by these tests for Cs, Sr, U and Nd are 0.01, 0.1, 1×10^{-4} and 3×10^{-4} g/m^2 · d, respectively, by day 15. Difference between SYNROC leach rates measured using monoliths vs. crushed samples are explained on the basis of inaccurate geometric surface area measurements.

THE APPLICATION OF MÖSSBAUER SPECTROSCOPY TO THE CHARACTERIZATION OF NUCLEAR WASTE FORMS. Paul G. Huray, M. T. Spaar, S. E. Nave, and J. M. Legan, University of Tennessee Physics Department, Knoxville, Tennessee 37916 and Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830 and L. A. Boatner and M. M. Abraham, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830

The Mössbauer isotopes ^{57}Fe and ^{237}Np have been employed in quantitative examination of in situ fractions of these nuclei present in mixed atomic environments in a variety of waste forms. An identification of the electronic charge states and site symmetries produced from the Mössbauer isomer shifts and electric field splittings allow stoichometry to be determined in many cases. The effects of heat treatment, reducing atmosphere, and preparation procedure were investigated for iron in: a. synthetic monazite and zircon i.e. the entire rare earth orthophosphate series (excluding promethium), b. tetragonal YPO_4 and $ScPO_4$, c. $Th_3(PO_4)_4$ with ThP_2O_7, d. high iron simulated Savanah River Waste (SRW) in $LaPO_4$, e. $FePO_4 \cdot xH_2O$ and $Fe_3(PO_4)_2 \cdot 8H_2O$, f. high iron SRW in SYNROC via a Sol-Gel sphere procedure, g. synthetic perovskite - $CaTiO_3$, and h. a series of Borosilicate glasses including Fe_2O_3, high iron SRW, and standard MCC 76-68 glass. The effects of preparation procedure and temperature have been investigated for neptunium in $LaPO_4$ and following α-recoil implantation for ^{241}Am in $LaPO_4$. The latter study providing an analysis of radiation damage within microseconds of formation of a given local atomic environment.

Research sponsored by the U.S. Dept. of Energy under contracts DE-AS05-79ER10348 with the University of Tennessee and W-7405-eng-26 with Union Carbide Corporation.

PHOTOEMISSION STUDY OF LEACHED 76-68 WASTE GLASS SURFACES. D. P. Karim, D. J. Lam, H. Diamond, A. M. Friedman* (Argonne National Laboratory, Argonne, IL 60439), D. G. Coles, F. Bazan (Lawrence Livermore Laboratory, Livermore, CA 94720) and G. L. McVay (Battelle Pacific Northwest Laboratory, Richland, WA 99352)

Samples of 76-68 simulated waste glass containing U, Np, and Pu have been examined using x-ray photoemission spectroscopy to monitor changes in the surface composition resulting from leaching. Significant differences in composition are seen among samples leached in distilled water, salt brine, and 0.04 N bicarbonate solution. Other leaching variables examined include temperature and flow rate. In addition, a group of samples leached under anoxic conditions were studied and shown to exhibit systematic differences in surface composition compared to those samples leached in the presence of air.

*Work supported by the U.S. Department of Energy.

B1 THE USE OF ^{222}Rn AS A FLOW PATH MONITOR FOR STUDIES OF RADIONUCLIDE TRANSPORT IN FISSURES*. J. Hines, D. Cohen, S. Fried, and A. Friedman, Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439.

A technique has been developed using ^{222}Rn as a flow path monitor. Its principle advantage over other radiotracers or dyes is that while the Kd of Rn gas in water solution is zero and hence follows the water path, its ^{210}Pb daughter is retained strongly by rock. The immobilized ^{210}Pb is not subject to diffusion, an important consideration in the proposed Nevada Field Test. To evaluate the technique, a series of laboratory scale experiments have been performed. Artificial fissures consisting of glass plates and prepared flat rock surfaces were coupled to insure well characterized fissures. Water solutions of Rn were metered through these fissures and the discharge monitored to produce breakthrough curves as a function of flow rate. The rock surfaces were analyzed for radionuclide concentration and the rock sectioned for diffusion profile into the rock. Comparison to theoretical models have been made for each parameter.

*Work performed under the auspices of the United States Department of Energy under contract number W-31-109-ENG-38.

B2 FORMATION AND PROPERTIES OF AMERICIUM COLLOIDS IN AQUEOUS SYSTEMS. U. Olofsson, B. Allard, K. Andersson and B. Torstenfelt, Department of Nuclear Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden.

The formation of americium colloids in aqueous solutions has been studied with variation of the americium concentration, pH, ionic strength, time and temperature, and some properties of the colloid particulates (size and charge) have been estimated.

The sorption of americium colloids on some solids has been studied as well as the mobility of americium on montmorillonite pseudocolloids. The potential release and transport of americium and other trivalent actinides from an underground repository for radioactive waste and the possibility of obtaining an enhanced mobility due to the formation of true colloids or pseudocolloids are discussed.

B3 SITE CHARACTERIZATION FOR FIELD RADIONUCLIDE MIGRATION STUDIES IN CLIMAX GRANITE, Dana Isherwood, Ellen Raber, and Randolph Stone, Lawrence Livermore National Laboratory, Livermore, CA 94550.

Radionuclide migration experiments in fractured granite at the Climax Stock, Nevada Test Site, are needed to compare field and laboratory measured retardation factors to determine whether laboratory studies accurately reflect in situ conditions. Initial field activities have concentrated on hydrological investigations to determine whether the fractures in Climax granite are suitable for migration experiments. A critical question was whether we could isolate a single vertical fracture between two boreholes and establish flow along that fracture from an upper to a lower borehole. At three sites, pairs of 76 mm (NX) holes were drilled about two meters apart. The holes were oriented to intersect sets of high angle vertical fractures at approximately right angles. Inflatable straddle packers were used to isolate individual fractures. Of the ten fractures tested to date, one fracture would not take water at pressures up to 200 psi for 24 hours. Several fractures were either so permeable they exceeded the pumping capacity of the equipment or else failed to show a connection between the two boreholes. In two fractures, we were able to establish a circulating system with up to 95% of the injected water recovered. Constant pressure injection tests and pulse tests were conducted. Fracture transmissivities of 5×10^{-4} and 1.4×10^{-3} m^2/day were calculated using a radial flow model. Effective fracture apertures were estimated at 20 and 30 mu m. Concurrent with the hydraulic testing activities is a study of the Climax groundwater chemistry. Our analyses show the natural water to be very different in composition from the equilibrated granitic water usually used in laboratory sorption studies. This paper will describe the results of the hydrogeological and geochemical investigations, and overall experimental design plans for the radionuclide migration experiment to be conducted next year.

NUCLIDE MIGRATION FIELD EXPERIMENTS IN TUFF, G-TUNNEL, NEVADA TEST SITE,*
B. R. Erdal, R. S. Rundberg, K. Wolfsberg (Los Alamos National Laboratory), D. R. Fortney, K. L. Erickson (Sandia National Laboratories), A. M. Friedman, S. Fried, and J. J. Hines (Argonne National Laboratory).

A project to begin to address the phenomena of flow and element migration in fractured porous rock has recently been started by the Los Alamos National Laboratory, Sandia National Laboratories, and Argonne National Laboratory. The work has three objectives: 1) to develop the experimental, instrumental, and safety techniques necessary to conduct controlled small-scale radionuclide migration field experiments; 2) to use these techniques to define radionuclide migration through rock by performing generic, at-depth experiments under closely controlled conditions in a single fracture in porous rock; and 3) to determine whether available lithologic, geochemical, and hydraulic properties together with existing or developed transport models are sufficient and appropriate to describe real field conditions (i.e., to scale from laboratory studies to bench-size studies to field studies).

The experiments consist of several key elements. Among these are detailed groundwater characterization, including seeps in G-tunnel and local tuffaceous wells. Site selection will depend largely on fracture flow (permeability) tests. Two migration experiments will be performed. Stable or short-lived nuclides will be used in the first experiment, in part to demonstrate the safe experimental procedures for conducting the second, actinide-containing, experiment. Both experiments include detailed post-flow analyses of the fracture, radionuclide distributions, etc., since they are essential for correlating the migration of nuclides under actual conditions with laboratory and modeling studies. Comprehensive laboratory studies of the sorption and migration properties of the same materials are being performed using existing and newly developed bench-scale techniques.

*Work supported by the U. S. Department of Energy.

PREDICTING Pu CONCENTRATIONS IN SOLUTIONS CONTACTING GEOLOGIC MATERIALS.
Richard G. Strickert and Dhanpat Rai, Battelle, Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352

A specific solid phase, $PuO_2(c)$, has been shown to limit the concentration of plutonium in various aqueous solutions, including solutions contacting contaminated sediments and simulated glass waste forms. Measurements of the solubility of $PuO_2(c)$ as a function of pH over a 3-year period indicate that equilibrium solution concentrations of Pu are approached rather rapidly. Although sorption/desorption on solid materials may be occurring, Pu solution concentrations remain at levels predicted from the $PuO_2(c)$ solubility line. Alpha radiation has no significant affect on Pu solubility due to possible changes in crystallinity; however, alpha radiation induced production of HNO_3 increases the solution concentration of Pu and may affect Pu solution species.

This work was performed for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.

86 TRANSIENT HYDRAULIC TESTS IN GRANITE: FRACTURED POROUS MEDIUM ANALYSIS AND RESULTS.
John H. Black, and John A. Barker, Institute of Geological Sciences, Harwell Laboratory, Harwell, Oxfordshire, England

Slug and pulse tests have been used extensively to measure the hydraulic conductivity and specific storage of granitic rocks. After several hundred tests using our own design of straddle packer test equipment, it became clear that the conventional methods of test analysis were inadequate. The straddle packer equipment developed by IGS allows the time scale of test to be altered without repositioning the packers so that a range of tests can be carried out on the same test interval. The new analysis procedure presented combines porous rock, in which water storage occurs, with fissures, through which groundwater flow takes place. A new variable is introduced which includes the unknown parameters matrix hydraulic conductivity, matrix specific storage, fissure specific storage and fissure hydraulic conductivity together with the known or controllable variables, effective casing radius and packer interval length. Examples of analysis using multiple tests in the same interval are presented together with the apparent relationship between measured hydraulic conductivity and specific storage. It would appear that a small number of fractures endow the rock mass with the bulk of its hydraulic conductivity and that some field tests have measured matrix hydraulic conductivity at about 1×10^{-12} m sec^{-1}.

87 A NATURAL ANALOGUE FOR STORAGE OF RADWASTE IN CRYSTALLINE ROCKS,
Douglas G. Brookins, Mark S. Abashian, Dept. Geology, Univ. N.M., Albuquerque, NM 87131; Lewis H. Cohen, Univ. Calif., Riverside, CA 92502; Harold A. Wollenberg, Jr., Lawrence Berkeley Laboratories, Berkeley, CA 94720.

The Eldora-Bryan stock (Colorado) intruded the Precambrian Idaho Springs Formation metamorphic rocks 58 million years ago. Geochronologic-geochemical work by Hart et al. (1968) has demonstrated that the heat from the cooling intrusive rocks was sufficient to affect mineral isotopic systematics up to 2,000 m. from the contact, and the nature of these isotopic perturbations can be explained by a simple diffusion model in turn based on various heat flow models. Our new studies are focused on elemental exchange between stock and intruded rock as a function of distance from the contact; the assumption is made that the stock is a very large, high heat source analogous to a waste form emplaced in the metamorphic rocks without benefit of canister or engineered backfill. Data for U, Th and the REE indicate actinide and lanthanide immobility except perhaps in the 0-2 m. contact zone where some infiltration of the country rocks by stock-derived fluids occurred. Beyond 4 m. no stock-derived U, Th, REE or *Pb are noted. Further, whole rock Rb-Sr and stable O isotopic data indicate conductive cooling as opposed to convective, water-induced cooling. The intruded rocks possess low porosity and permeability; this helped prevent elemental migration during the 10^5 - 10^6 years of stock crystallization. The petrographic and geochemical studies show that the Idaho Springs (or equivalent) metamorphic rocks are well suited for radwaste storage.

RADIONUCLIDE MIGRATION: LABORATORY EXPERIMENTS WITH ISOLATED FRACTURES,* R. S. Rundberg, J. L. Thompson, and S. Maestas (Los Alamos National Laboratory).

Laboratory experiments examining flow and element migration in rocks containing isolated fractures have been initiated at Los Alamos National Laboratory. Techniques are being developed to establish simple fracture flow systems which are appropriate to models using analytical solutions to the matrix diffusion – flow equations, such as those of I. Neretnieks.[1] These experiments are intended to be intermediate steps toward larger scale field experiments where it may become more difficult to establish and control the parameters important to nuclide migration in fractured media. Hopefully, these experiments will validate the simple models and help to identify the more significant properties which need to be characterized in order to make accurate predictions.

Laboratory experiments have been run on fractures ranging in size from 1 to 20 cm in length. The hydraulic flow in these fractures was studied to provide the effective apertures. The flows established in these fracture systems are similar to those in the granite fracture flow experiments of Witherspoon et al.[2] Traced solutions containing ^{85}Sr and ^{137}Cs were flowed through a 15.6 μm fracture in Climax Stock granite. The results of the elution agree with a matrix diffusion calculation based on independent measurements of K_d and porosity. Similar experiments are currently underway on various rock types, including Climax Stock granite, Stripa granite, welded tuff (Tram member, Yucca Mountain, Nevada Test Site) and G-tunnel tuff (a highly zeolitized non-welded ash full tuff from the Nevada Test Site).

*This work was supported by the U.S. Department of Energy.

[1] I. Neretnieks, "Diffusion in the Rock Matrix: An Important Factor in Radionuclide Retardation?", J. Geophysical Research 85, 4379 (1980).

[2] P. A. Witherspoon, J. S. Y. Wang, K. Iwai, and J. E. Gale, "Validity of the Cubic Law for Fluid Flow in a Deformable Rock Fracture," Lawrence Berkeley National Laboratory Report (October 1979) LBL-9557.

EFFECT OF ORGANIC COMPLEXING AGENTS AND TEMPERATURE ON ADSORPTION OF RADIONUCLIDES: IMPLICATIONS FOR DISPOSAL OF RADIOACTIVE WASTE. A.Maest, S.Tréhu, E.Dillon, D.Crerar, Princeton Univ. Geology Dept. Princeton, NJ 08544; J.Means, Battelle-Columbus Labs.

Laboratory adsorption studies have been conducted using clays of varying cation exchange capacities and solutions containing an organic complexing agent (oxalic and gallic acids and EDTA at $2x10^{-3}$m) and four metals representative of nuclear waste: Cs,Sr,Co and U at $5x10^{-4}$m. Experiments were run from 25°-250°C in shaker baths and high T and P rocking autoclaves. The clay(mg) to solution(ml) ratios were 5:100, 1:100 and 0.5:100 for kaolinite, illite and montmorillonite respectively. The solutions were buffered at constant pH (pH=5.0 at 25°C). Adsorption onto the clays initially decreased with increasing temperature for all metals and then began to increase markedly at different temperatures, determined by the ionic radii and valencies of the metals. The adsorption increases for U,Co,Sr and Cs began at ~75°,100°, 150° and 200°C respectively and reached nearly 100% adsorption for all metals except Cs. We interpret this as the result of several competing mechanisms: an initial adsorption onto the clay's surfaces or in more internal, possibly Al, structural sites with later interlayer adsorption. Above 200°C the crystallinity of the clays is diminished, apparently opening more sites for adsorption. Results from solutions with complexing agents imply that they increase metal adsorption below their degradation temperatures (~100° for oxalic, 150° for gallic and 200°C for EDTA), possibly by creating a charge inbalance in the clays as a result of their high affinity for Al. Co, however was held strongly in solution with EDTA below the degradation temperature of the complexing agent the reached nearly 100% adsorption after the Co-EDTA complex broke down. Thermal degradation of chelating agents used in power plant clean-ups before burial with nuclear wastes would inhibit organically-bound radionuclides from remaining in solution and therefore increase the likelihood of sorption onto geologic media in the repository.

C1 DIFFUSION MEASUREMENTS IN COMPACTED BENTONITE. B. Torstenfelt, K. Andersson, B. Allard and U. Olofsson, Department of Nuclear Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden.

A cell for measurements of radionuclide diffusion in compacted clay has been designed. In this cell the diffusing element is introduced in the middle of a cylindrical clay body, and water is allowed to enter into the clay from both ends. From determinations of radionuclide concentration profiles in the clay diffusivities can be calculated, and the mass transfer rate of the radionuclide through compacted clay e.g. in a backfill barrier in a waste repository can be quantitatively described.

Diffusion data for some fission products and americium in compacted bentonite are given in the paper, and the possibilities of introducing additives to the clay that would enhance the retention of specific radionuclides, e.g. the actinides, are discussed.

C2 DISSOLUTION OF SIMULATED SPENT FUEL IN HYDROTHERMAL SOLUTION. W. Phelps Freeborn, Sridhar Komarneni, Barry E. Scheetz, and William B. White, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

Spent fuel is difficult to simulate because of the unique microstructure that develops in reactor fuel pellets. However, the chemical reaction of spent fuel and water should be amenable to investigation. Three compositions were prepared: pure $UO_{2.08}$, $UO_{2.08}$ plus 3.5 wt% simulated fission products (corresponding to 33,000 MWd/MTU burnup), and $UO_{2.08}$ plus 40 wt% simulated fission products. The fission products (19 elements) were mixed, fired in hydrogen to simulate appropriate reducing conditions, mixed with UO_2 and fired again in sealed capsules. These materials were reacted at 100°, 200° and 300°C with water, a saturated NaCl brine and a $MgCl_2/CaCl_2/KCl/NaCl$ bittern brine at 300 bars pressure for periods of time from 1 to 5 weeks. Product solids were examined by SEM and X-ray methods; product solutions were analysed for extracted uranium and fission product elements.

The resistance of UO_2 to solution, especially under reducing conditions, however, does not prevent the extraction of most of the fission product elements even at low temperatures. The alkali and alkaline earth elements are very readily extracted; effectively all of the cesium has been removed into solution at 200°C. Molybdenum and the rare earths are also extracted although less effectively while little zirconium is removed. A substantial amount of uranium is taken into solution presumably through an oxidation mechanism and by chloride complexing. The bittern brine is a more effective solvent than water and particularly so for uranium.

IIGRATION RATES OF BRINE INCLUSIONS IN SINGLE CRYSTALS OF NaCl. I-Ming Chou, U.S. C3
eological Survey, 959 National Center, Reston, VA 22092.

ock-salt deposits have been considered as a possible medium for the permanent
torage of high-level radioactive wastes and spent fuel. Brine inclusions present
n natural salt can migrate if the temperature gradients in the vicinity of the
adioactive waste are large enough. In order to better assess the problem, the
iigration rate of these brine inclusions must be esimated under various repository
onditions. Among the existing models of the migration process, the one presented
y Anthony and Cline (1971, J. Appl. Phys. 42, 3380-3387) is considered as being
he most complete, because it accounts for most of the phenomena known to occur in
he migration process. However, application of their model is difficult because of
n insufficient data base. By utilizing recent data for halite saturated brines and
he model of Anthony and Cline, the effect of brine composition on the migration
ate of inclusions was evaluated at 50° and 100°C. Because Soret coefficients (σ)
f salt in brines are not known, the Soret coefficient must be treated as a variable.
n order to simplify the calculation, the interface kinetics are neglected. Then
he isothermal maximum migration rate predicted by Anthony and Cline's model reduces
o a simple linear function of σ for each brine composition. Although the estimated
aximum migration rates for WIPP-A, NRT-6, and 2.41 m $MgCl_2$ brines are of the same
rder of magnitude, they differ markedly from those of pure NaCl solution (except in
narrow region of σ values). At 100°C, these calculated migration rates are
onsiderably higher than those measured experimentally. This discrepancy indicates
ither that the neglected interface kinetics or the presence of a gas phase in the
easured inclusions might be important retarding factors for the migration rates of
nclusions, or that the model used is not perfect.

ORROSION OF STRUCTURAL MATERIALS IN CLAY ENVIRONMENTS, J. Dresselaers, F. Casteels, C4
H. Tas, SCK/CEN, Metallurgy B.2400 Mol, Belgium.

Disposal of radioactive waste in stable geological formations is presently considered
as one of the most safe methods for the isolation of radionuclides contained in the
waste from the ecosphere. In Belgium the use of a geological clay formation is
studied for the burial of radioactive waste.

The corrosion rate and mechanism of construction materials of galleries and casings
for boreholes (eventually to be used as consumable overpack for 12 HLW canisters) has
been evaluated after corrosion experiments in direct contact with clay, in a humid
clay atmosphere and in a gas corrosion chamber. The experiments in direct contact
with clay have been carried out "in situ" and in closed stainless steel cylinders.

The experiments have been carried out in the temperature range between 13°C (tempera-
ture of the clay formation) and 70°C.

The exposed specimens consists of a series of alloyed and non-alloyed cast nodular
irons protected with different anti-corrosive protections (hot dipping, paintings,
plastics, bitumen).

The experiments lasted up to several years.

The corrosion attacks are interpreted in terms of the Cr, Ni and Si content of the
alloyed cast nodular irons and the weight, adhesion and porosity of the coating.

The aggressiveness of the different clay environments is interpreted in terms of the
presence of corrosive anions and cations and characteristics of the clay such as elec-
trical resistivity, pH, redox potential and redox capacity, sulphide and moisture con-
tent, bacterial activity and the nature of corrosive products escaping from the clay
under influence of a temperature effect.

C5 THE DISSOLUTION OF IRRADIATED FUEL UNDER HYDROTHERMAL CONDITIONS. L.H. Johnson, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba. ROE 1LO

Uranium dioxide, the major component of irradiated CANDU fuel, shows good hydrothermal stability under the appropriate redox conditions. The thermodynamic stability of UO_2 in brine and in low ionic strength granite groundwater at 150°C under oxidizing and reducing conditions is briefly reviewed in order to provide a basis for the discussion of results of irradiated fuel dissolution experiments. Fuel chemistry characteristics that influence the kinetics of fission product release are also discussed.

Experimental studies have demonstrated the influence of redox chemistry on irradiated fuel dissolution rates at 150°C, where matrix dissolution rates are decreased by a factor of 10-100 times in going from oxidizing to reducing conditions. Under oxidizing conditions, UO_2 matrix dissolution rates are not strongly temperature dependent. Observed rates, inferred from ^{90}Sr release to solution, indicate that the rate increases by a factor of about 10 between 25 and 150°C. These studies have indicated the need for further work in certain areas, in particular on the relative amounts of important fission products released through leaching and matrix dissolution.

C6 RETARDATION, PERMEABILITY, AND SWELLING OF CANDIDATE BACKFILL MATERIALS, J. H. Westsik, Jr., L. A. Bray, F. N. Hodges, and E. J. Wheelwright, Battelle Pacific Northwest Laboratory, Richland, WA 99352

Batch distribution coefficients (Kd) for I-125, Sr-85, Cs-137, and Tc-99, with candidate backfill material and synthetic Grande Ronde groundwater have been measured for contact times up to 28 days. The results show that cesium and strontium are retained by the clays and zeolites (Kd - 10^{-10}). Iodine was retained by silver-treated Na-bentonite (Kd = 270), and technetium was not retained on any material tested.

Selected flow-through experiments have been directed at evaluating sodium and calcium bentonite clays and clay/sand mixtures. Synthetic Grande Ronde groundwater shows a significant change in composition as cations and anions are being sorbed and/or released during flow through the clay/sand compacts.

Hydraulic conductivities and swelling pressures are being determined as functions of the density of the compacted backfill, temperature, radiation dose, hydraulic head, the chemical composition of the permeating fluid. Bentonite clays and bentonite/sand mixtures have received initial emphasis in the program. For samples compacted by the same pressure, the hydraulic conductivity increased and the swelling pressure decreased as sand content increased in the mixture. In experiments using synthetic Grande Ronde groundwater, sodium bentonite has shown the lowest hydraulic conductivity of 7×10^{-13} cm/sec. Calcium bentonite has a hydraulic conductivity roughly twice that of the sodium bentonite. A 1:1 mixture of sodium bentonite and 80-120 mesh quartz sand had a hydraulic conductivity of 4×10^{-12} cm/sec, and a 1:3 clay/sand mixture had a hydraulic conductivity of 7×10^{-10} cm/sec. In all cases the measured density was 2.1 g/cm^3.

PNL-SANDIA HLW PACKAGE INTERACTIONS TEST: PHASE ONE. Martin A. Molecke, Sandia National Laboratories, Albuquerque, New Mexico 87185, Don J. Bradley and John W. Shade, Battelle Pacific Northwest Laboratory, Richland, Washington, 99352

The first phase of a high-level waste (HLW) package interactions test in a salt environment has been completed. The test system consisted of PNL 76-68 HLW glass (loaded with inactive fission products and ^{238}U) surrounded by a stainless steel waste canister, a TiCode-12 overpack, a bentonite/sand backfill, excess brine leachant, and a bedded rock salt container, all held within a 19-liter autoclave. All components were physically compromised in order to force wasteform-barrier-salt geology interactions to occur during this 95-day, 250°C overtest. The empirical test data obtained (analyses of leachant and all barrier surfaces) will be compared with supporting data from simpler test systems previously conducted. Contrary to previous predictions, the glass wasteform did not totally dissolve under the severe overtest conditions. The data presented will be used to predict interactions and performance under realistic salt repository environmental conditions.

8 EXPERIMENTAL STUDIES OF PROCESSES GOVERNING THE RELEASE AND SUBSEQUENT SORPTION OF NUCLIDES IN GRANITE REPOSITORIES. N. A. Chapman, P. J. Dudson, I. G. McKinley, D. Savage and J. M. West, Institute of Geological Sciences, Harwell Laboratory, Harwell, Oxfordshire, England

Progress over the last 18 months in laboratory and modelling studies of near-field behaviour in a granite repository is reviewed. Data are presented on the hydrothermal interactions of glass and granite, and the factors controlling the release source term. These include temperature dependent solubility of the glass and leachability of various nuclides, availability of groundwater, and formation of a crystalline secondary waste form. Estimates are made of release rates of significant nuclides to the rock. Data are presented on the interaction of Cs, Ce, Sr and Co with weathered granite, replicating altered fissure surfaces. The conventional K_D assumptions are replaced by parameters reflecting dependency of sorptive behaviour on temperature, concentration, pH and reaction direction. A simple model is used to demonstrate a means of synthesising these hydrothermal and waste-rock interaction data. Data suggest that disposal at temperatures initially in the order of 200°C may be feasible.

DEGRADATION OF ROCKS, THROUGH CRACKING CAUSED BY DIFFERENTIAL THERMAL EXPANSION, IN RELATION TO NUCLEAR WASTE REPOSITORIES. R.W. Davidge, J.R. McLaren and I. Titchell, Materials Development Division, AERE Harwell, OX11 ORA, U.K.

Heating to moderate temperatures, 50-500°C, gives a significant reduction in Young's modulus of rocks and it is likely that a major reason is grain boundary cracking. The cracking of grain boundary facets in polycrystalline multiphase materials showing anisotropic thermal expansion behaviour is controlled by several microstructural factors in addition to the intrinsic thermal and elastic properties. Of specific interest are the relative orientations of the two grains meeting at the facet, and the size of the facet; these factors thus introduce two statistical aspects to the problem. The criteria for facet fracture are critically reviewed. The statistical factors are then introduced to give quantitative data on crack density versus temperature. The theory is compared with the limited experimental measurements of Young's modulus for various rocks as a function of temperature. There is good qualitative agreement, and the additional (mainly microstructural) data required for a quantitative comparison is defined. Comment is made about the relevance of the effects to underground nuclear waste repositories.

C10 DEVELOPMENT OF ENGINEERED STRUCTURAL BARRIERS FOR NUCLEAR WASTE PACKAGES. Richard E. Westerman, Stanley G. Pitman, and Rebecca P. Elmore, Pacific Northwest Laboratory, Richland, Washington, 99352.

A program directed toward the development of licensable structural engineered barrier elements for long-lived nuclear waste packages has been underway at PNL since January, 1979. Emphasis is currently placed on metallic materials for canister, overpack, and hole sleeve applications. These barrier elements are expected to contribute substantially to a barrier system that will hold radioisotope release rates to near-zero values for time periods of approximately 1000 years.

The development of structural barriers involves the initial selection of candidate materials; their screening by means of mechanical and corrosion testing; their rigorous in-depth testing in repository-relevant environments, using accelerated tests that can be extrapolated to long time periods; and ultimately, their evaluation in conjunction with other package elements in site-equivalent environments for final package qualification.

Corrosion screening of alloys in 250°C autoclave tests, with basaltic groundwater environments, constitutes a major part of the program effort, with cast irons and cast steel presently receiving the most attention. The stress corrosion cracking of alloys is being investigated in basaltic groundwater by means of slow-strain-rate tests and cyclic loading of pre-cracked specimens. Emphasis is placed on titanium alloys in these studies.

E1 A STUDY OF ZIRCONOLITE FROM SRI LANKA AND SOUTH AFRICA. Richard F. Haaker, Rodney C. Ewing, Department of Geology, University of New Mexico, Albuquerque, NM; Thomas J. Headley, Sandia National Laboratory, Albuquerque, NM.

The long-term stability of radioactive waste forms such as SYNROC are difficult to assess from leaching and irradiation experiments which are of limited duration. One approach to the evaluation of crystalline radioactive waste forms is to examine the chemical alteration and radiation effects in natural materials of great age. Since natural analogues are the product of a long-term experiment, they may serve as useful standards against which the results of short-term experiments can be compared. Specimens of zirconolite from Sri Lanka and South Africa have been characterized by optical microscopy, TEM, SEM, the electron microprobe and x-ray diffraction. Both zirconolites are partially metamict but the original structure is restored by heating in air (1130°C - 4 hours). Optical examination of the Sri Lanka zirconolite suggests that little chemical alteration has occurred. Since the South African zirconolite is intergrown with other minerals, an estimate of the degree of alteration from optical data is difficult. SEM and TEM studies indicate that the Sri Lanka zirconolite has 1 micron and smaller spherical pores, perhaps due to helium accummulation. Similar porosity was not detected in the South African zirconolite. Both zirconolites have regions of crystalline and amorphous material. Optical, TEM, SEM, microprobe and x-ray diffraction data are presented and discussed. In light of these data, the long-term stability of zirconolite is evaluated. Limitations on the use of natural analogues for the prediction of long-term effects in synthetic phases are addressed.

E2 WITHDRAWN

(PERIMENTAL AND THEORETICAL ANALYSES OF SMALL-SCALE RADIONUCLIDE MIGRATION FIELD
(PERIMENTS,* K. L. Erickson and D. R. Fortney, Sandia National Laboratories,**
lbuquerque, New Mexico, 87185.

ecently completed analyses define criteria for selecting sites for small-scale
adionuclide migration field experiments and for choosing optimum experimental con-
itions for analysis of fundamental processes dominating radionuclide migration.
etailed characterization of geomedia and experiments to identify dominant chemical
henomena were used to develop a mathematical model for migration in an idealized
oint in nonwelded tuff. The model was applied to a hypothetical experiment. Criteria
or optimum operating conditions were developed in terms of the physical and chemical
arameters of the system, and effects of perturbations in parameter values were
xamined. The principal results of these analyses will be summarized. For example,
f sorption occurs by a process such as ion exchange, the parameters dominating
adionuclide transport in jointed rock are the sorption equilibrium distribution co-
fficient, the plate spacing of the joint, and the average fluid velocity. The
riteria for optimum operating conditions will be described using these parameters,
nd it will be shown that perturbations in the fluid velocity and plate spacing would
ave a larger impact on experimental results than the distribution coefficient. The
nalyses are being evaluated experimentally, and initial results are encouraging.
he experiments will be described, and available data discussed. Much of the work
nder consideration also would be applicable to other types of jointed rock, and
xamples will be given to illustrate how the physical and chemical properties of the
ock could affect experimental results. Extension of the small-scale analyses to
arger joint systems also will be considered.

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* A U. S. Dept. of Energy facility.

EFERENCE LABORATORY TESTING FOR BACKFILL, Riley M. Chung and Felix Y. Yokel,
eotechnical Engineering Group, Structures and Materials Division, Center for
uilding Technology, National Bureau of Standards, Washington, D.C. 20234

elatively high magnitude of swelling and low hydraulic conductivity are two of
he performance requirements for the backfill placed around the radioactive waste
ackage for the underground nuclear waste storage scheme. Some studies have been
onducted in national laboratories and in other countries where the candidate
ackfill materials were tested under many different conditions to determine the
expected range of these properties.

This paper briefly examines the variables that can be significant in the eval-
uation of these two properties and emphasizes the ones, including compaction
effort, methods of specimen compaction, and the moisture content at the time
of compaction, which for one reason or another have not been considered in the
test programs.

E5 STUDIES OF LOCALIZED CORROSION AT HIGH TEMPERATURES OF PIT AND CREVICE MICRO-ENVIRONMENTS. V. Kay Hardman and Jerome Kruger, National Bureau of Standards, Bldg. 223, Rm. B254, Washington, DC 20234.

Studies of canister materials in nuclear waste repository environments have been undertaken to determine the susceptibility of these materials to localized corrosion for long times (> 1000 years). Since the local environments in pits and crevices can differ greatly from that found in the bulk solution, electrochemical and pH measurements in these microenvironments are taken to determine the corrosion rate and passive regions of stainless steel and Ti alloy materials. These metals are tested in sodium ion solutions with various concentrations of chlorine ions simulating possible environments found in nuclear waste repository sites. Repassivation properties of these materials are examined by scratch tests at several temperatures between 25 and 200°C.

This work is partially supported by the Office of Nuclear Waste Management.

E6 STRONTIUM-BASALT REACTIONS UNDER NUCLEAR WASTE REPOSITORY CONDITIONS. Sridhar Komarneni, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

Hydrothermal interactions of Sr as strontium chloride or hydroxide with basalts or basalt phases were investigated at 300°C for 4 and/or 12 weeks under a confining pressure of 30MPa. The nature and extent of Sr immobilization varied with the Sr source and with the basalt or basalt phase as determined by the characterization of solid and solution reaction products. Basalts or basalt phases immobilized up to 99% of the added Sr. The main mechanism of Sr fixation with basalts or basalt phases excepting with the glass phase seems to be ion exchange when $SrCl_2$ was the Sr source. However, when $Sr(OH)_2$ reacted with basalts or basalt phases Sr was immobilized by the crystallization of strontium aluminosilicates such as $SrAl_2Si_2O_8$. These results of Sr-near-field interactions in a basalt repository indicate that basalt can be a good barrier for Sr migration from nuclear wastes.

E7 BACKFILL-WASTE INTERACTIONS UNDER RADWASTE REPOSITORY CONDITIONS. Noriaki Sasaki, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-Mura, Ibaraki-Ken, Japan; Sridhar Komarneni, Barry E. Scheetz and Rustum Roy, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

Alteration of backfill materials such as montmorillonite and clinoptilolite with and without the presence of simulated nuclear waste solids such as borosilicate glass, glass ceramic, sintered ceramic and supercalcine ceramic was investigated under hydrothermal conditions of 300°C and 300 bars for 4 weeks. Experiments were conducted under dry as well as wet repository conditions. Montmorillonite and clinoptilolite did not seem to alter under both dry and wet repository conditions as determined by XRD. However, the above backfill materials altered extensively in the presence of various simulated wastes under both dry and wet repository conditions. Backfill materials mainly altered to feldspar (oligoclase) in the presence of borosilicate glass and to analcime in the presence of sintered ceramic under both dry and wet repository conditions. Montmorillonite did not alter either in the presence of glass ceramic or supercalcine ceramic under both dry and wet repository conditions. However, clinoptilolite altered to analcime in the presence of glass ceramic or supercalcine ceramic under wet repository conditions. The above reactions of backfill materials with simulated wastes immobilized waste elements such as Cs, Mo, etc. by forming new phases such as analcime, oligoclase and powellite. In fact, analyses of product solutions from interaction runs indicated that the presence of backfill materials during the alteration of waste solids served to immobilize many waste elements. These results show that backfills can be effective barriers for nuclide migration if they come in contact with the wastes during the thermal period of the life of a repository.

_PHA DECAY SELF-DAMAGE IN CUBIC AND MONOCLINIC ZIRCONOLITE. F. W. Clinard, Jr., . C. Land, D. E. Peterson, D. L. Rohr, and R. B. Roof, University of California, os Alamos National Laboratory, Los Alamos, NM 87545.

he zirconolite phase of the SYNROC waste form will be a host to actinide isotopes hich generate self-damage by alpha decay. Natural zirconolite is often found in he partially-metamict condition from self-damage over geologic times. In this ondition the mineral exhibits a defect fluorite cubic structure which transforms o the normal monoclinic form on heating.

tudies are under way to investigate accelerated damage in zirconolite by doping ith $^{238}PuO_2$ (half-life=88 y). Samples containing 25 mol % PuO_2 in place of the 5 mol % ZrO_2 constituent have been fabricated and the resulting material, which s fluorite cubic, stored at ambient temperature for 200 days. Macroscopic welling saturated at 4.6 vol % at a dose of 1.8×10^{19} α decays/cm^3, while X-ray welling saturated at 2.2 vol % and 6×10^{18} α/cm^3. Aging studies are also being arried out on 5 mol % PuO_2--20 mol % ZrO_2 zirconolite, which is primarily onoclinic. Macroscopic swelling at 3×10^{18} α/cm^3 is approximately the same as hat for the cubic form. Other physical property observations for these materials, uch as degree of metamictization, defect content, fractographic characteristics, nd extent of microcracking, will also be described. Results are compared with hose obtained by others from natural and neutron-irradiated synthetic irconolite.

HEMICAL, PHYSICAL, AND ENGINEERING CHARACTERIZATION OF CANDIDATE BACKFILL CLAYS ND CLAY ADMIXTURES FOR A NUCLEAR WASTE REPOSITORY. Dr. S.K. Singh, President, aterials Research Laboratory Ltd., 98 Caesar Avenue, Nepean, Ontario K2G 0A8.

he investigation includes the characterization of Fourteen Canadian Clay and Clay dmixtures on the basis of their mineralogic, chemical, physical and engineering ehaviour under simulated environments of a nuclear waste repository located in a ranitic pluton.

he experimental data obtained during the study warrants further research on elected samples to prepare composites suitable for backfill and buffering purposes.

ADIATION INDUCED SODIUM METAL COLLOID FORMATION IN NATURAL ROCK SALT FROM SEVERAL EOLOGICAL LOCALITIES*--J. M. Loman, P. W. Levy and K. J. Swyler, Brookhaven ational Laboratory, Upton, New York 11973

he principal radiation damage induced in natural rock salt from various localities, including potential repository sites, consists of point defects and, in the 115 to 250C range, colloidal sodium metal particles. With increasing dose the radiation induced point defects, primarily F centers, grow to a saturation level, which is reached at doses of 10^7 to 10^8 rad, and that decreases with increasing temperature to a negligible level at 300C. Colloid growth follows a nucleation and grow curve accurately described by a $C(dose)^n$ expression at large times. For numerous natural rock salt samples irradiated at 150C, the temperature of the maximum colloid formation rate, the exponent n lies between 1.5 and 2.3 and the constant C varies by a factor of more than 30. The constant C, which is a measure of the total colloid that would be formed in a given repository, is related to the sample strain and the impurity and void content. The currently available data indicates that repository rock salt adjacent to planned waste canisters will develop 0.001 to 0.1 mole percent sodium.

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E11 STUDY OF POLYHALITE FROM THE WIPP SITE, NEW MEXICO. Douglas G. Brookins, Dept. of Geology, University of New Mexico, Albuqerque, NM 87131.

Polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$) is an important mineral present in the bedded evaporites of the WIPP site, southeastern New Mexico. Because of the two structurally bonded molecules of water, it is important to know if this mineral formed at the time of evaporite formation or, as proposed by Tremba (1969) and Bodine (1978), much later and more or less continuously in post-evaporite time. If the latter mode of information is the case, then this implies a source of new water in order for polyhalite to form; in turn raising serious questions about water mobility and abundance in the bedded evaporites in the post-Late Permian. Polyhalite is not well suited for Rb-Sr geochronology as it contains too much common Sr; but it has been shown to be well suited for K-Ar geochronology (Brookins et al., 1980). Samples of polyhalite representing very pure material, mixtures with halides (NaCl and KCl), from xenoliths from rubble chimneys, from distorted layers near rubble chimneys, and from the recrystallized contact zone of a 33 MYBP lamprophyre dike have been studied. The K-Ar apparent ages range, for pure polyhalite, from 190 - 216 MYBP whereas impure polyhalites range from 155 - 205 MYBP. Both show a correlation of K-Ar age lowering as a function of halide content and, when age vs. % Na (proportional to halide content) plots are used, extrapolated ages of formation of 220 - 235 MYBP are obtained. These data convincingly show that the polyhalites formed at the time of sedimentation, except for the dike contact zone material, and not at much younger times (op. cit.). Finally, petrographic and thermodynamic information show that polyhalite is earlier than carnallite and some sylvite, which supports the K-Ar information.

E12 URANIUM-LEAD RADIOMETRIC AGE DETERMINATIONS OF NATURALLY OCCURRING U(VI) MINERALS: APPLICATION TO RADWASTE STORAGE. Douglas G. Brookins, Dept. Geology, Univ. of New Mexico, Albuquerque, NM 87131.

U(VI) bearing species are commonly formed under laboratory rock-water-HLW experimental conditions. Artificially produced Na-Cs-Rb weeksite (alkali uranyl hydrosilicate), and other U(VI) species, may be metastable for the Eh-pH conditions under which the chemical reactions may take place; and it is not known from the experimental work if these species will be subjected to alteration such that U is released. To address this problem naturally occurring U(VI) bearing minerals (uranophane and tyuyumanite) from the Grants mineral belt, New Mexico, have been studied for their U-Pb systematics. Samples from highly oxidized rocks and from overall chemically reducing environments have been studied. The samples from oxidized rocks are mixed with hematite-barite-gypsum-calcite-kaolinite gangue whereas those from reduced rocks are mixed with goethite-calcite gangue and are close to, but not in contact with, pyritiferous-organic carbon-uraniferous (U(IV))-chloritic ore. The reduced rock uranophane yields nearly concordant $^{238}U - ^{206}Pb$ and $^{235}U - ^{207}Pb$ ages of 8.32 and 8.33 MYBP (millions of years before the present); the oxidized rock uranophane and tyuyumanite yield more discordant ages (n = 8) between 7.4 and 2.7 MYBP. These data argue for long range stability of U(VI) hydrosilicates under both oxidizing and reducing conditions and imply that U(VI)-rich phases produced during experimental rock-water-HLW reactions are also stable under a wide range of Eh in the pH range of interest.

DIFFUSION OF NEPTUNYL(V)- AND PERTECHNETATE IONS IN MARINE SEDIMENTS*. F. Schreiner, S. Fried, and A. Friedman, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.

The diffusion of the $^{235}NpO_2^+$ and $^{95m}TcO_4^-$-ions has been measured directly in sample cylinders of two different sediments from the floor of the deep sea. In smectite-rich sediment not shielded from contact with atmospheric oxygen the following values were obtained for the effective diffusion coefficients of neptunyl- and pertechnetate-ions, respectively: $D_{eff}(NpO_2^+) = 1.5 \times 10^{-12} m^2 s^{-1}$ and $D_{eff}(TcO_4^-) = 3.2 \times 10^{-11} m^2 s^{-1}$. Under anoxic conditions in sediment with known reducing properties, the pertechnetate ion appears to undergo slow reduction and the effective diffusion coefficient of the reduced species of $D_{eff}(Tc,red) = 1.1 \times 10^{-14} m^2 s^{-1}$ reflects a substantial decrease of the mobility of the lower-valent technetium.

*Work performed under the auspices of the Sandia National Laboratory Program Contract #74-1160.

RADIOGEOLOGICAL ASSESSMENT OF CANDIDATE SITES FOR NUCLEAR WASTE REPOSITORIES, EXEMPLIFIED BY STUDIES OF THE STRIPA PLUTON, SWEDEN. H. A. Wollenberg, S. Flexser and L. Andersson, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

Investigation of candidate sites for nuclear waste isolation will require an assessment of their radiogeologic settings. Studies at the Stripa research facility in granitic rock of central Sweden incorporated the distribution and abundance of naturally occurring radioelements in rocks encompassing the underground experiments and in the accompanying fracture-controlled groundwater system. These studies showed that besides defining the natural radioactivity baseline upon which the effects of radioactive waste will be superimposed, radioelement distributions can be used to determine the apparent age of the groundwater and its flow paths. In crystalline rocks, where the groundwater systems are confined to the joints and fractures, the uranium daughter element, radon-222 in the water serves as a natural tracer to locate fractures along which significant flow is occurring and to measure the flow rates. The heat production from radioactive decay of uranium-238, thorium-232 and potassium-40 in the rock, combined with measurements of regional and local geothermal heat flow, permit calculation of the apparent size of the rock mass that will encompass the repository. This method is especially useful in terranes such as at Stripa where the contacts between plutons and older rocks are concealed.

NOVEL EXPERIMENTS FOR UNDERSTANDING THE SHALLOW LAND BURIAL OF LOW-LEVEL RADIOACTIVE WASTES. Gerald L. DePoorter, Los Alamos National Laboratory, Environmental Science Group, Los Alamos, NM 87545

Data on the basic processes that occur in the shallow land burial of low-level radioactive wastes are needed to engineer facilities with guaranteed performance, to validate models for system predicitons, and to provide input to models that consider contaminant pathways out of the facility. Two types of novel experiments that are providing experimental data on the basic processes in shallow land burial facilities are described in this paper. Generic experiments that give data on the movement of water and radionuclides and an experiment that is particularly important for semi-arid sites are described.

E16 IDENTIFICATION OF POSSIBLE HIGH INTEGRITY CONTAINERS FOR NUCLEAR WASTE DISPOSAL, J. Williams, Hittman Nuclear & Development Corporation, 9190 Red Branch Road, Columbia, MD 21045.

Increased concern by the State of South Carolina over the condition and capacity of the low-level radioactive waste burial site at Barnwell has prompted them to promulgate new regulations on waste burial containers. As of September 30, 1981, ion exchange resin and filter media waste with an activity of 1 uCi/cc or greater, or longer than five-year half-life isotopes disposed of at Barnwell, shall be solidified or confined in a "high integrity container." The materials and designs of these containers are required to provide waste isolation from the environment for a period of 300 years, and provide the structural integrity specified in 49 CFR 173.398. HITTMAN has been active in the design and development of containers suitable for this purpose with this paper detailing the analyses involved. Material selections were limited to stainless steel, fiberglass, and polyethylenes. Structural concerns focused on overpressure requirements, drop-testing requirements, and lifting capabilities. With a lifetime dose of up to 10^8 rads, the possibilities of radiation damage were considered. Preliminary selection of polyethylene was based on satisfactory resolution of these issues and economic factors. A brief discussion of the regulatory process encountered in this project is also included.

E17 PREDICTIONS OF RADIONUCLIDE MIGRATION RATES FOR A SUBSEABED REPOSITORY. Laurence H. Brush, Seabed Programs Division 4536, Sandia National Laboratories Albuquerque, NM 87185

Geochemical research supporting the U. S. Subseabed Disposal Program is described. Data from studies of high temperature interactions between sediments and porewater (seawater), and of sorption and diffusion of radionuclides in oxidized deep sea sediments are used, along with results from heat transfer studies, to predict migration rates of radionuclides in a subseabed repository.

Preliminary results for most radionuclides in oxidized sediments are very encouraging: fission products with moderate values of K_D (generally 10^2 to 10^5), and actinides with high values of K_D (generally 10^3 to 10^6) would not migrate significant distances before decaying to innocuous levels. ^{137}Cs, ^{90}Sr, and ^{239}Pu are among this group. The results for anionic species in oxidized sediments are less encouraging, but preliminary work with reduced sediments indicates that Tc can be effectively isolated.

Planning for a field verification of these laboratory and modeling studies is also described.

STOCHASTIC ANALYSIS OF GROUNDWATER FLOW AND CONTAMINANT TRANSPORT IN A FRACTURED ROCK SYSTEM. F. W. Schwartz, Dept. of Geology, Univ. of Alberta, Edmonton, Canada, L. Smith, Dept. of Geological Sciences, Univ. of British Columbia, Vancouver, Canada and A. S. Crowe, Dept. of Geology, Univ. of Alberta, Edmonton, Canada.

It has been possible to develop a stochastic model for groundwater flow and transport in a fractured rock system. Using a Monte Carlo method, a large number of statistically independent realizations of a fracture network are generated from a single set of distributions on parameters defining the fracture geometry. These parameters are the number of fractures, their location, orientation, length and aperture. By solving for hydraulic head at the fracture intersections, and using data on fracture aperture and porosity, seepage velocities may be calculated and the transport equation solved for each realization using a moving particle technique. Output from the Monte Carlo simulation consists of distributions on concentrations and various exit times. The applications are specifically designed to highlight the usefulness of the modeling concept. One very important application is to investigate the validity of the equivalent porous medium concept and the diffusional model of dispersion which are key assumptions in conventional continuum models. In addition, we illustrate the variety of plume shapes which can develop in fractured systems, and examine how parameters of fracture geometry act to control transport.

SOLIDIFICATION OF RADIOACTIVE WASTES WITH THERMOSETTING RESIN. M. Hayashi[1], K. Kobayashi[2], O. Okamoto[3], T. Kagawa[4], K. Wakamatsu[5], H. Irie[6], H. Matsuura[7], and Y. Nakayama[7]. Tokyo Electric Power Co.[1]; Tohoku Electric Power Co.[2]; Chubu Electric Power Co.[3]; Chugoku Electric Power Co.[4]; Japan Atomic Power Co.[5]; Toshiba Corp.[6]; NAIG Lab.[7]; Japan.

Dried simulated radioactive wastes were solidified with thermosetting resin and their properties were investigated with laboratory scale and real scale products through extensive testings; mechanical resistance, resistance to leaching and swelling in water, radiation resistance, fire resistance, resistance to temperature cycle. The typical results were as follows: over 500 kg/cm^2 of compressive strength, 10^{-6} -- 10^{-5} cm^2/day of diffusion constant for ^{137}Cs leaching from concentrated wastes solidified products, no remarkable change up to 5×10^8 RAD irradiation, thermal damage limited to the surface after the thermal test of IAEA transportation guide.

NUCLEAR WASTE DISPOSAL: THE INTERFACE BETWEEN PERFORMANCE ASSESSMENT AND RESEARCH R.B. Lyon, Whiteshell Nuclear Research Establishment, Atomic Energy of Canada Ltd., Pinawa, Manitoba ROE 1LO

The potential impact of the post-closure phase of a nuclear fuel waste disposal project is radiation dose to man. Radiation dose is estimated as the end product of a total systems analysis. Field and laboratory research must be assimilated in a form which can be accepted by the total systems analysis procedure. A central focus of this assimilation must be the consideration of uncertainties in the analysis and data used. Irreducible uncertainty arises because of the wide variability in natural systems and the unprecedented extrapolation into the distant future.

A procedure called systems variability analysis, incorporated in the SYVAC computer program, provides a framework for assimilation of the results of the field and laboratory research with a systematic treatment of uncertainty.

A SYVAC assessment of the post-closure performance of a Canadian nuclear waste disposal facility is presented with particular illustrations of the interface between the assessment models and data, and the field and laboratory research.

F4 PROCESSING OF TITANATES AND ZEOLITES, AND USE OF A CARTRIDGE SYSTEM FOR "REACTOR" WASTES, S. Forberg, T. Westermark, K. Svärdström, RIT, Stockholm; and L. Fälth, LIT, Lund, Sweden.

Hot isostatic pressing, hot uniaxial pressing, and cold pressing followed by simple sintering were technically compared as methods for conditioning of titanates and zeolites with radioactive and corrosion products having been transferred from organic ion exchangers, used for parallel purification of PWR water.

The pre-pressing conditioning, i.e. pre-heating, of the inorganic ion exchangers was studied, e.g. the bulk density obtained and the limitations from volatilization of radioactive species.

The density, the crystallographic composition and the leachability at Soxhlet tests and in cold (40°C) granitic ground water were studied.

Aiming at a simple, hygienic and fool-proof handling of radioactively charged inorganic ion exchangers, a cartridge system was designed for the whole route from packing of channel-free beds, via charging and emptying of the columns, to drying and preheating of the beds, and packing of the canisters for final conditioning (hot isostatic or hot uniaxial pressing or sintering).

After suitable measures, HLW trapped in titanate in such cartridges could form bodies with rutile as a continuous matrix and as a protective outer layer, a MEGANNITE, with an optional million-year warranty.

F5 PERFORMANCE OF ASPHALT AND CLAY LINERS AS A URANIUM MILL TAILINGS LEACHATE BARRIER. J. L. Buelt, V.Q. Hale and S. M. Barnes, Pacific Northwest Laboratory, Richland, Washington 99352.

Pacific Northwest Laboratory is evaluating the long-term effectiveness of various asphalt and clay liner materials as a radionuclide and process chemical barrier from uranium mill tailings. A field test is being conducted by monitoring asphalt and clay liners installed at the Grand Junction, Colorado tailings site. In addition eight prospective liners have undergone three months exposure to accelerated conditions to predict their behavior over a 1000 year period. High calcium leachates have been forced through thin layers of clay to determine the ability of the clay to resist ion exchange, which reduces its swelling capabilities. Asphalt liners are being exposed to elevated temperatures and increased strengths of oxidizing agents to accelerate their aging processs. The permeability coefficients measured during this exposure is then used to predict the expected lifetime. The analyses thus far show that clay soils with bentonite amendments and most asphalt compositions have good long-term performance characteristics.

EHAVIOR OF RADIONUCLIDES IN FUSED WASTE-DISPOSAL-SITE SOIL PRODUCED BY IN-SITU ITRIFICATION,* C. L. Timmerman, and J. L. Ruelt, Pacific Northwest Laboratory, ichland, Washington 99352

Radioactive wastes buried at waste disposal sites may require further stabilzation to secure the isolation of these wastes from the environment. One method of aste stabilization proposed is in-situ vitrification. In-situ vitrification is the n-place melting of the soil and encapsulation of the wastes in this molten soil to orm a glass and crystalline waste form. This paper will present analytical results nd predictions pertaining to the behavior of radionuclides in fused soil.

Solidification of contaminated soil is achieved by establishing an electric urrent between electrodes placed in the soil. The electric current produces a oule-heating effect that melts the soil and immobilizes any contaminants. Benchcale demonstrations of this concept with soil contaminated with nonradioactive esium, strontium, and ruthenium were performed. These demonstrations have provided preliminary indication of migration effects, off-gas contamination potential, and levitrification predictions. In addition to the nonradioactive data and tests, a rucible-scale melt of soil spiked with radioactive uranium, plutonium, and cesium as been leach tested. These nonradioactive and radioactive test results show good adionuclide retention in the fused soil, which indicates an excellent potential for pplication of in-situ vitrification to burial wastes and contaminated soils at aste disposal sites.

*Work performed for the U. S. Department of Energy under Contract DE-AC06-76RLO 1830

A COMPARATIVE ASSESSMENT OF TRU IMMOBILIZATION SYSTEMS - W. A. Ross, C. O. Harvey. R. O. Lokken, R. P. May, F. P. Roberts, C. L. Timmerman, R. L. Treat, and J. H. Westsik, Jr., Battelle-Pacific Northwest Laboratory, Richland, WA, 99352.

The results of a comparative assessment of six alternative TRU waste forms and seven processes for application at Rocky Flats will be reported. This assessment has the objective of evaluating both waste form containment properties and economics and safety of processes. The waste forms which are being evaluated include cast cement, pressed cement, borosilicate glass, aluminosilicate glass, sintered ceramics, and basalt glass ceramics. The waste forms have been prepared with sludge and plutonium containing incinerator ash from Rocky Flats. The waste form properties which are being evaluated include leachability, impact behavior, pressurization potential, and thermal stability. The waste form processes which are being evaluated for a new facility at Rocky Flats include batch cement mixing, cement mixing and pressing, in-can melting, joule heated melting, glass marbles, basalt glass ceramics, and pressed and sintered ceramics. The overall economics are based on capital cost, operating costs, D & D costs, transportation costs, and repository disposal costs. The importance of occupational exposure, industrial hazards, criticality safety, and quality assurance are also being determined.

F8 LOW-LEVEL WASTE DISPOSAL RISK ANALYSIS, S.G. Oston, C.M. Koplik, D.A. Ensminger, J.Y. Nalbandian, M.F. Kaplan, The Analytic Sciences Corporation, One Jacob Way Reading, Massachusetts 01867

The Analytic Sciences Corporation (TASC) is assessing the safety of low-level waste disposal. A computer code, LOTRAN, is under development to model the various pathways along which radionuclides can reach man via inhalation, ingestion, and direct exposure to gamma rays. These pathways include contaminated river water, well water, airborne dust, locally grown crops, and radon diffusion. The study considers the geologic and hydrologic properties of the disposal site and the properties of engineered barriers such as trench liners, caps, tailored waste forms, and high integrity containers used to inhibit the release of radionuclides.

Radiation doses to off-site individuals and to future land reclaimers are computed for a number of generic disposal sites located in both dry and humid environments. The predicted doses are to be compared to illustrative performance criteria developed under this project and to draft NRC criteria. Results will provide insight into those characteristics of low-level waste disposal systems most important to public safety and will allow trade-offs to be performed among natural and engineered features.

F9 LEACH STUDIES OF RADIONUCLIDES FROM SOLIDIFIED WASTES WITH THERMOSETTING RESIN. Kazunori Suzuki and Hiroshi Kuribayashi; JGC Corporation, Wataru Morimitsu and Isamu Ono; Industrial Research Institute of Kanagawa, Yokoham, Japan.

In Japan, low and intermediate-level radioactive wastes generated in nuclear power plants are solidified with cement or asphalt. Meanwhile, solidification processes using thermosetting or thermoplastic resin have recently been developed and are attracting much attention from the standpoints of volume reduction , immobilization of radionuclides and the physical and chemical qualities of the solidified products.

We, in collaboration with CEA/ECOPOL(France), have investigated and developed a new solidification process using thermosetting resin. This paper reports studies on the leachabilities of Co-60 and Cs-137 from speciemens solidified with thermosetting resin and evaluates the effects of chemical fixations on leach rate. This study concludes that insolubilization by nickel-ferrocyanide offers an effective chemical fixation of those radionuclides and is a recommendable pretreating method for radiowastes to be solidified.

PROCESSING TAILORED CERAMIC NUCLEAR WASTE FORMS, J. Flintoff, D. R. Clark, A. B. Harker, P. E. D. Morgan, and C. M. Jantzen, Rockwell Science Center.

Tailoring of Savannah River Defense Waste into a four-phase assemblage can be accomplished with minimal tailoring by hot isostatic pressing (HIPping). A fully dense fine grain ceramic is produced with chemical host sites for all radionuclides and no continuous glassy phases present. The tailoring formulations and resulting phase assemblages are given. The phases produced all have natural mineralogic analogues which are known to be geologically stable.

Processing of SRL Defense Waste into a ceramic monolith with the desired combination of mineralogic phases is dependent on the tailoring additives, redox control and consolidation conditions. Optimally, the Fe^{+3}/Fe^{+2} ratio should be <2/1 to take maximum advantage of the elemental content of the waste while uranium is desired to be in the tetravalent state. Use of wet chemical reducing agents before cold compaction avoids powder handling problems. The reduction occurs at 250°C and the redox control of the phase development has been examined at a sequence of temperatures up to 1200°C. Samples produced by this method show the same phases as ceramics made by calcining and reduction at the Fe/FeO buffer before and after final consolidation.

ON-LINE MEASUREMENTS OF THE VOLATILIZATION OF RUTHENIUM IN A VITRIFICATION PROCESS, R. Odoj, KFA-ICT, Postfach 1913, D-5170 Julich, FRG.

In the course of high level waste solidification, the volatilization of ruthenium causes some problems. Two mechanisms of release are possible: mechanical entrainment of particles and volatilization of constituents. To measure both factors, the investigations were carried out on-line with radioactive Ru103 als tracer.

Preliminary work indicates very low volatility at temperatures 100°C. Between 100°C and 200°C, the main fractional release of ruthenium takes place and amounts to more than 10%. Even at high temperatures during the glass melting, the fractional release was lower. The overall release of ruthenium during concentration, calcination and glass melting was about 16%. Denitration before calcination reduces the release of ruthenium about one order of magnitude. By adding iron powder as an additional agent, the volatilization was futher decreased even below 0.5%. The studies indicate that there should be other mechanisms and compounds besides the vaporization of RuO_4, which are responsible for the volatilization of ruthenium. The volatility of ruthenium in nitric acid solution is proportional to the volatilization of NO_3 — at temperatures of 100°C. This result is not related to the equilibrium vapor pressure of RuO_4 in this range of temperature.

CEMENTITIOUS RADIOACTIVE WASTE HOSTS FORMED UNDER ELEVATED TEMPERATURES AND PRESSURES (FUETAP CONCRETE), L. R. Dole, J. G. Moore, G. C. Rogers, G. A. West, H. E. Devaney, W. T. Morgan and J. H. Kessler, Chemical Technology Division, Oak Ridge National Laboratory, P. O. Box Y, Oak Ridge, TN 37830.

Concretes formed under elevated temperatures and pressures (FUETAP concretes) are effective hosts for transuranic (TRU) and high-level defense and commercial wastes.

Tailored cement formulations developed at ORNL use Portland cement, fly ash, sand, and clay additives. These FUETAP concretes are cured under mild autoclave conditions then dewatered to remove the unbound water. The resulting solids are strong (60-100 MPa, compressive strength), leach resistant (Pu at a rate of 10^{-11} g/cm^2-d) and radiolytically stable (lambda total = 0.005 molecule/100 eV) monolithic waste hosts.

This paper summarizes the results of the four-year old FUETAP development program. These continuing studies give data addressing the major questions concerning radioactive waste forms. These are: (1) leachability, (2) radiation stability, (3) thermal stability, (4) thermal conductivity, (5) impact strength, (6) permeability, (7) phase complexity and (8) effect of waste composition.

G4 BEHAVIOR OF RADIONUCLIDES AT SMELTING OF NONCOMBUSTIBLE SOLID WASTES. M. Osaki and S. Yokoi, Daido Steel Co., Ltd., Mutuno, Atuta-ku Nagoya Japan and M. Miyagawa, The Chubu Electric Power Co., Thoshin-cho, Higashi-ku Nagoya Japan.

Melting process of noncombustible solid wastes seems one of the most promising processes in point of volume reduction and immobilization. We have been developing the melting furnace of noncombustible solid wastes. However, melting process needs high temperature around 1500 °C, but the behavior of radionuclides in such process and at such temperature has not been fully examined. In part of developing stage, we melted small contaminated samples to examine the behavior of radionuclides. And melted samples were presented to leaching tests.

Samples were carbon steel, SUS304, silicaboard, concrete and zeolite and melted by laboratoryscale plasma arc melting furnace. After melting, radioactivity of melted samples and dusts were counted to calcurate the distribution of radionuclides. Melted samples were submerged to estimate leaching rate.

Many assorted samples were melted and we found that the vapour pressure of radionuclide determined the distribution between melted products and dusts. The standerd free energy of oxide formation and the quantity of stable nuclide of that radionuclide determined the distribution between metal and slag products. Leaching rate of melted products were sufficient low.

These works have been developed by Chubu, Tohoku, Tokyo, Kansai and Chugoku Electric Power Companies, Japan Atomic Power Co. and Daido Steel Co.

G5 VITRIFICATION OF HIGH-LEVEL RADIOACTIVE WASTE IN A SMALL-SCALE JOULE-HEATED CERAMIC MELTER. Gerald B. Woolsey, Russell E. Eibling, and Lien-Mow Lee, E.I. duPont de Nemours & Co., Savannah River Laboratory, Aiken, SC 29808.

Vitrification in borosilicate glass is the current reference process for the immobilization of Savannah River Plant high-level radioactive waste. Much of the chemistry and the design data for the process have been developed using experiments with nonradioactive, simulated waste. To demonstrate the equivalence of radioactive and simulated waste in the process, an integrated, shielded process has been constructed on a small scale at the Savannah River Laboratory. This process has established the equivalence of actual and synthetic waste in the reference process and yielded information on off-gases which was not readily accessible with simulated waste. This paper presents the results of vitrification studies on actual waste fed as a water slurry directly to the glass melter.

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G6 METASTABLE LIQUID IMMISCIBILITY IN NUCLEAR-WASTE-GLASSES. John E. Engell and G. Roed, Institute of Mineral Indystry, The Technical University of Denmark, DK-2800 Lyngby, Denmark.

Changes in chemical durability of borate glasses upon phase separation is well-known. A similar behaviour of nuclear waste-glasses is clearly unwanted. The data presented concern potential nuclear-waste-glasses containing 9 wt% of simulated fission products and presently under consideration by the Swedish Nuclear Energy Association (KBS/SKBF). The glasses have compositions closely related to the ternary system Na_2O-B_2O_3-SiO_2. In this system a broad spectrum of glass compositions show metastable phase separation upon heat treatments in the range 550°C to 775°C. The 600°C-isotherm for the extension of this immiscibility dome into the multi-component system relevant to nuclear-waste-glasses has been located experimentally. The results give the lower limit for the alkali oxide content in useful waste-glasses of this type.

MERCURY REDUCTION AND REMOVAL DURING HIGH-LEVEL RADIOACTIVE WASTE PROCESSING AND VITRIFICATION.* Russell E. Eibling and John R. Fowler, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, SC 29808.

At the Savannah River Plant, a process for immobilizing the high-level radioactive waste in borosilicate glass has been developed. This waste contains a substantial amount of mercury from separations processing. Since mercury will not remain in borosilicate glass at the processing temperature, mercury must be removed either before vitrification or must be handled in the off-gas system. A process has been developed to remove mercury by reduction with formic acid prior to vitrification. Studies with both simulated and actual waste are discussed. Additional benefits of formic acid treatment include improved sludge handling and glass melter redox control.

*The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

INTERIM WASTE FORMS FOR HIGH-LEVEL RADIOACTIVE WASTES: PROCESSING AND PROPERTIES,* G. Bandyopadhyay and S. M. Gehl, Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

Several interim waste forms have been investigated in the laboratory using simulated materials to study their suitability for application in handling and transportation of high-level radioactive wastes to terminal processing sites. In the fused-salt/sludge option, the neutralized supernatant liquid and the precipitated sludge are treated simultaneously to form fused-salt cakes. Silicate-based options, in which sodium silicate or cement-silicates act as binders for the calcined sludge, require prior separation of the sludge and the soluble radioactive constituents from the supernatant before the waste form can be prepared. The results from tests on simulated fused-salt waste forms indicated that the process simplicity of this option is partially offset by the high water solubility and hygroscopicity, which would make special precautions necessary during transportation and storage. The most promising silicate-based option is the cement-silicate process, in which the sludge is mixed with sodium silicate and $Ca(OH)_2$ powder and subsequently exposed to a controlled-humidity environment at room temperature to form the cementitious bond. Waste forms containing up to 90 wt % synthetic sludge and with sufficient mechanical and chemical stability have been prepared by the cement-silicate process.

*Work supported by the U. S. Department of Energy.

H3 IMMERSION AND LEACH TESTS ON SOLIDIFIED DECONTAMINATION WASTES FROM UNIT 1.* Robert E. Barletta, J. W. Adams, and R. E. Davis, Division Waste Management, Brookhaven National Laboratory, Upton, NY 11973

In order to provide technical support to the NRC, Brookhaven Na Laboratory has performed leach tests and immersion tests using organic liquids and organic saturated water of concentrated decontamination waste solidified using a vinyl ester-styrene binder.

The leach tests measured the release of Fe, Ni, and Co from these forms in deionized water, groundwater, and seawater. After 64 days, the mean fraction released normalized by V/S for iron was $5.1 \pm 1.9 \times 10^{-3}$ cm in deionized water, $7.1 \pm 1.1 \times 10^{-3}$ cm in groundwater, and $1.0 \pm 3.2 \times 10^{-3}$ cm in seawater. For nickel, 64 day release rates observed were $4.6 \pm 1.6 \times 10^{-3}$ cm, $4.6 \pm 1.0 \times 10^{-3}$ cm, and $5.9 \pm 0.6 \times 10^{-3}$ cm in deionized water, groundwater, and seawater, respectively. After 50 days, the ^{59}Fe release rates are $5.9 \pm 0.7 \times 10^{-3}$, $4.8 \pm 2.4 \times 10^{-3}$, and $2.8 \pm 1.0 \times 10^{-3}$ cm in deionized water, groundwater, and seawater, respectively. For ^{60}Co, the 50 day releases in the three respective leaching media are $6.0 \pm 1.7 \times 10^{-3}$ cm, $6.8 \pm 1.0 \times 10^{-3}$ cm, and $2.3 \pm 0.2 \times 10^{-3}$ cm.

Immersion tests of waste forms prepared at a solidification demonstration held at the Dresden Nuclear Power Station were conducted in toluene, xylene, and water saturated with toluene and xylene. Upon immersion of samples in the pure organics, large changes in sample volume and weight were observed. Total weight changes upon immersion of $9.6 \pm 0.3\%$ and $21.6 \pm 0.7\%$ were observed after 839 hours of immersion in xylene and toluene respectively. Air drying of the samples led to an overall weight loss of $23.5 \pm 0.7\%$ for xylene and $35.6 \pm 0.6\%$ for toluene. Qualitatively, similar changes were observed for immersion tests using organic saturated water. Severe sample deterioration was observed in this case, however. The cause of this deterioration is not known.

*Work carried out under the auspices of the Nuclear Regulatory Commission.

H4 TAILORED ION EXCHANGE RESINS FOR COMBINED CESIUM AND STRONTIUM REMOVAL FROM SOLUBLE DEFENSE HIGH-LEVEL WASTE*. Martha A. Ebra and Richard M. Wallace, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, SC 29808.

Novel organic resins that achieve high selectivities for both cesium and strontium have been synthesized. They are condensation polymers of resorcinol and formaldehyde with attached chelating groups. Their column performance compares favorably with that of commercially available resins for either cesium or strontium removal. By combining Cs^+ and Sr^{2+} removal in the same bed, these resins can significantly reduce the size and complexity of proposed facilities for processing defense high-level waste.

*The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

H5 BIOLOGICAL INTRUSION OF LOW LEVEL WASTE TRENCH COVERS-T.E. Hakonson, Environmental Science Group, Los Alamos National Laboratory, Los Alamos, NM 87545

The long-term integrity of low-level waste shallow land burial sites is dependent on the interaction of physical, chemical, and biological factors that modify the waste containment system. Past research on low-level waste shallow land burial methods has emphasized physical (i.e. water infiltration, soil erosion) and chemical (radionuclide leaching) processes that can cause waste site failure and subsequent radionuclide transport.

The purpose of this paper is to demonstrate the need to consider biological processes as being potentially important in reducing the integrity of waste burial site cover treatments. Plants and animals not only can transport radionuclides to the ground surface via root systems and soil excavated from the cover profile by animal burrowing activities, but they modify physical and chemical processes within the cover profile by changing the water infiltration rates, soil erosion rates and chemical composition of the soil. Examples of the effects plants and animals have in modifying soil profiles are drawn from the ecological literature and from operating low-level waste sites where plants and animals have caused radionuclides to be transported from the waste trenches.

One approach to limiting biological intrusion thru the waste cover is to apply a barrier within the profile to limit root and animal penetration with depth. Experiments in the Los Alamos Experimental Engineered Test Facility were initiated to develop and evaluate biological barriers that are effective in minimizing intrusion into waste trenches. The experiments that are described employ four different candidate barrier materials of natural geologic origin. Experimental variables that will be evaluated, in addition to barrier type, are barrier depth and soil overburden depth.

H6 STABILITY OF I AND SR RADIOPHASES IN CEMENT MATRICES, M.W. Barnes, B.E. Scheetz, L.D. Wakeley, S.D. Atkinson and D.M. Roy, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

The following study is a portion of a comprehensive research program that is examining the stability of a variety of nuclear waste forms. In addition to the bulk waste forms, important individual radiophases are being studied to obtain a more complete understanding of the behavior of the components of complex multiphase radwaste systems. The stability of the Sr-radiophase in supercalcine ceramic and a I-radiophase will be discussed.

The strontium radiophase in this study was a Sr-powellite and the iodine radiophase was I-sodalite. Each radiophase was incorporated into bulk compositionally adjusted portland and aluminate cements. Two processing variables were studied: curing at 60°C and warm pressing at 150°C and 345 MPa.

The I-sodalite appears to approach congruent dissolution in the portland cement. However the mechanism is masked by the presence of Na, Al, and Si in the aluminate cement. Soxhlet leach rates for I^- are 5 and 7.5 $gm^{-2}d^{-1}$ at three weeks in the aluminate and portland cement respectively. The Sr-powellite leaches incongruently at short times but the mechanism appears to change and trends to congruent dissolution with increasing leachtimes.

H7 THE SYSTEM $SrMoO_4$-$BaMoO_4$-$CaMoO_4$: COMPATIBILITY RELATIONS, THE IMPLICATIONS FOR SUPERCALCINE CERAMICS. Barry E. Scheetz, W.P. Freeborn, J. Pepin and W.B. White, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

The stability of the tailored ceramic waste form designed for high level commercial nuclear waste was examined under hydrothermal conditions. This study indicated that the phase with the scheelite structure, dissolved and reprecipitated. The compositions of the initial and final phases were different, although of the same structure. A schematic phase diagram was proposed to explain the observations.

This study is then the experimental determination of those phase relations. Samples were heated following the schedule for the supercalcine ceramic. Characterization of these runs by x-ray diffraction suggests that the two phase region between the calcium and barium end members extends into the ternary system to about sixty weight per cent of the strontium end member.

Hydrothermal treatment of critical compositions at 300°C resulted in further separation of the compositions of the coexisting phases.

The change in composition observed in the previous work is thus confirmed to be due to the instability of the intermediate compositions formed at high temperature at the lower temperatures of the hydrothermal treatment.

H8 IRON-ENRICHED BASALT AND ITS APPLICATION TO THREE-MILE ISLAND AND WEST VALLEY RADIOACTIVE WASTE DISPOSAL. P. V. Kelsey, Jr., J. M. Welch, D. E. Owen, and J. E. Flinn, EG&G Idaho, Inc., P.O. Box 1625, Idaho Falls, ID 83415

Demonstration tests have been performed with iron-enriched basalt (IEB) as a dissolution/immobilization medium for some TMI and West Valley rad-waste disposal needs. Zeolite used for Cs and Sr decontamination of TMI containment water was mixed and melted with 20 wt. % additives to form IEB. Studies show that low Cs volatility during melting can be expected. The Cs leach rate from controlled-cool monoliths is 4×10^{-6} $g/cm^2 \cdot d$ (in 263 K deionized water). Dissolution of simulated TMI reactor core debris (UO_2 pellets clad with zircaloy) in IEB occurred in 2 h at 1773 K.

Simulated calcine from the neutralized high-level liquid waste stored at West Valley, N.Y., was incorporated into IEB at 25, 35, and 50 wt. % loadings. Leach tests on the resultant waste form materials showed no dependence on waste loading.

H9 LEACHING STUDIES OF Na-BEARING CRYSTALLINE PHASES IN NUCLEAR WASTE FORMS. E.R. Vance and T. Adl, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

Since the most soluble element in nuclear waste forms will likely be Na, various possible Na-bearing crystalline phases which might occur in nuclear waste forms were studied. The following phases were investigated for leach behavior in various aqueous media: $NaAlSiO_4$, $NaNbO_3$, $Na_{0.5}La_{0.5}TiO_3$, $NaFeSi_2O_6$, $NaZr_2(PO_4)_3$, $NaFeO_2$, Na_2TiSiO_5, $Na_2Ti_3O_7$, $Na_5Ti_8O_{14}$, $Na_2Ti_2Si_2O_9$, Na_2ZrSiO_5, $Na_2ZrSi_4O_{11}$, $Na_4Al_3Si_3O_{12}X$ (X = Cl or I) and $(Cs,Na)AlSi_2O_6 \cdot xH_2O$.

Ease of ceramic synthesis and the likelihood of the various phases actually occurring in crystalline nuclear waste forms are discussed.

0 IMMOBILIZATION AND LEAKAGE OF KRYPTON ENCAPSULATED IN ZEOLITE AND GLASS, J. E. Tanner, J. A. Del Debbio, A. B. Christensen, and D. A. Knecht, Exxon Nuclear Idaho Company, Inc.

Federal regulations will limit release of krypton-85 to the environment due to reprocessing of nuclear fuel irradiated after January 1, 1983. Immobilizing krypton in a solid may offer significant safety advantages over high pressure gas cylinder storage. High pressure/temperature encapsulation of krypton in zeolite 5A and "thirsty" Vycor glass results in typical loadings of 50 STP cc/g for zeolite and 20 STP cc/g for glass. Below 825°C, krypton leakage measured by thermogravimetric analysis (TGA) is 1-3% for zeolite 5A and less than 1% for glass.

Under 1000 atm of krypton optimum encapsulation temperatures are 700°C for zeolite 5A and 900°C for glass. Initial water loadings of 6 wt % or greater causes recrystallization to an anorthite type feldspar resulting in no krypton entrapment.

The final waste form was characterized by x-ray diffraction, differential thermal analysis (DTA), infrared and transmission electron microscopic techniques.

Leakage into vacuum of krypton trapped in zeolite 5A or porous Vycor "thirsty glass" is reported for temperatures of 500-800°C. The krypton is initially forced in at 1000 atm, and trapped by sintering at 700°C (zeolite) or 900°C (glass). A small amount, <2% in a well-prepared sample, is evolved in a few hours at 300-500°C. Leakage of the remainder is very slow. Extrapolation of leakage measurements over a few days or weeks at temperatures of 600-750°C to longer times and lower temperatures yields 13% leakage in 10 years at 600°C or 1.3% at 500°C. Above 800°C the structure breaks down in a few hours, and rapid leakage continues even after the temperature is lowered.

1 SOLUBILITY EFFECTS IN WASTE GLASS/DEMINERALIZED WATER SYSTEMS. Harold T. Fullam, Battelle, Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352.

A study was carried out to determine the solubility limits of various elements found in waste glasses in demineralized water as a function of temperature. The work was sponsored by the Office of Nuclear Waste Isolation under contract to the Department of Energy. Solubility measurements were carried out at 35°, 65°, 95° and 150°C using four nonradioactive waste glass compositions. Subsaturation and supersaturation methods were used to determine the solubility limits. The two methods gave markedly different values for most glass components. The results obtained indicate that it is impossible to assign solubility limits to most glass components without thoroughly describing the glass-water system. This includes not only defining the glass type and initial solution composition and temperature, but also the glass surface area-to-water volume (S/V) ratio of the system and its thermal history.

H12 THE IMMOBILIZATION OF CARBON-14 FORMED DURING REACTOR OPERATIONS*. Sherman Fried, Felix Schreiner, Donald Cohen, John Hines and Arnold Friedman, Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439.

Carbon-14 is formed during reactor operations by various nuclear reactions. During fuel reprocessing, decommissioning, or other operations this radionuclide is released to the atmosphere largely as $^{14}CO_2$ and will enter the biosphere through plant metabolism, animal respiration or through the water supply. Thus carbon-14 is considered to form a definite airborne biological hazard.

Carbon dioxide has been passed over hot magnesium turnings at approximately 600°C. The reaction

$$CO_2 + 2\,Mg \longrightarrow 2\,MgO + C$$

takes place readily and elemental carbon is deposited on the magnesium. Since carbon is both very inert and very insoluble (deposits of graphite have existed unchanged for hundreds of millions of years) this reaction provides a good method of immobilizing ^{14}C in a geological repository. By disposing of the ^{14}C in this manner it can be assured that ground water intrusion cannot mobilize it and carry it into the biosphere.

*Work performed under the auspices of the United States Department of Energy under contract number W-31-109-ENG-38.

H13 LANTHANIDE ORTHOPHOSPHATES AS A MATRIX FOR SOLIDIFIED RADIOACTIVE DEFENSE AND REACTOR WASTES.* M. Petek, M. M. Abraham, and L. A. Boatner, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

The lanthanide orthophosphates are being evaluated as a waste form for the storage of high-level defense and nuclear power reactor wastes. Pure lanthanum orthophosphate was employed as the host material for the incorporation of simulated composite Savannah River waste (SRW) without aluminum removal and simulated PW-4b reprocessed LWR wastes. In both cases the solidified waste forms were prepared from a nitric acid solution of the mixed, calcined simulated waste oxides and La_2O_3. The composite phosphate material was formed by the addition of $(NH_4)_2HPO_4$ or by combining $(NH_4)_2HPO_4$ with precipitation from molten urea. In the case of SRW the effects of waste loading (10 to 50 wt. % simulated SRW relative to La_2O_3) on the sintering properties of the composite material and on the formation of other crystalline phases were investigated. Dilatometry measurements on cold-pressed powders of the SRW material showed that sintering occurs in the range of 700 to 1000°C. Cold-pressed, sintered pellets of the SRW composite material had densities of 3.9 and 3.2 g/cm^3 for loadings of 20 and 50 wt. % SRW, respectively. In the case of $LaPO_4$ plus simulated PW-4b, the effects of urea precipitation conditions on the particle size and compaction properties were studied. Waste form pellets with 92 ± 2% of the theoretical density of pure $LaPO_4$ were formed by cold pressing and sintering (T_{max} = 1200°C) Hot pressing at 4000 psi and 1050°C produced pellets with a density of 96% of the theoretical value. Leaching results for Cs, Sr, and U will be presented.

*Research sponsored by the Division of Materials sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

4 HOT-PRESSED BARIUM SULPHATE CERAMICS FOR IMMOBILISATION OF MEDIUM LEVEL MAGNOX WASTE. A. Briggs, D.V.C. Jones and G.B. Cole, Materials Development Division, AERE Harwell, OXTI ORA, U.K.

A possible method of treatment for Magnox waste is by dissolution in nitric acid and conversion to barium sulphate floc by floc precipitation. Radwaste ions are co-precipitated with the floc.

This paper describes the results of work aimed at conversion of barium sulphate floc, containing simulated radwaste, into a synthetic, ceramic version of the natural mineral barytes by a hot-pressing route. By variation of the parameters pressure, temperature and time, optimum conditions for consolidation of the floc to > 90% theoretical density on a laboratory scale are found to be 22.5 MPa, 900°C for 10 minutes. Using these conditions, hot-pressed billets of $BaSO_4$ have been made on a 5 kg scale. In going from the Magnox sludge to the hot-pressed barium sulphate a volume reduction factor $\sim$ 50 is achieved. The principal phases in the product are found to be $BaSO_4$, MgO and Fe_3O_4, and the degree of consolidation achieved depends on the MgO content.

The leaching behaviour of the hot-pressed materials in 100°C, 3 day Soxhlet tests also depends on the MgO content, and on the consequent level of open porosity. If there is porosity accessible to the leach water, MgO at the internal surfaces is converted to $Mg(OH)_2$, which deposits within the pores, and a weight gain is registered in the Soxhlet test. If, however, there is no open porosity, a weight loss occurs, and leach rates $\sim 4 \times 10^{-7}$ kg/m^2/sec are found. In contrast, pure $BaSO_4$, hot-pressed to similar densities, shows no variation in leaching behaviour over a wide range of open porosities, and gives Soxhlet leach rates $\sim 8 \times 10^{-7}$ kg/m^2/sec. Leaching tests of both pure $BaSO_4$ and floc containing simulated radwaste, spiked with ^{137}Cs and hot-pressed under conditions giving similar densities, show that ...

5 IMMOBILIZATION OF HIGH LEVEL NUCLEAR REACTOR WASTES IN SYNROC: A CURRENT APPRAISAL A.E. Ringwood, V.M. Oversby and S.E. Kesson, Research School of Earth Sciences, Australian National University, Canberra, A.C.T. 2600, Australia.

Leaching tests carried out under dynamic rather than static conditions provide the best available means of predicting the comparative performances of wasteforms buried in a geological repository. Glasses dissolve quasi-congruently whereas leach rates obtained for the titanate ceramic wasteform SYNROC fall of drastically with time. Leach rates also vary considerably according to the species monitored. In water at 95°C the long-term leach rates of Cs, Ca and U from SYNROC are respectively 500, 2500 and 100,000 less than those from borosilicate glass. Even more pronounced differences prevail at 200°C and 300°C.

The effects of radiation damage on SYNROC minerals have been investigated. Natural zirconolites and perovskites have quantitatively retained α-emitting radionuclides even after radiation doses far greater than SYNROC would receive over a million years.

New developments in processing technology, to be described, make SYNROC manufacture simpler, less hazardous and probably less costly than borosilicate glass fabrication.

H16 THE INFLUENCE OF GAMMA IRRADIATION ON THE LEACHING BEHAVIOR OF MODIFIED SYNROC-B CERAMIC WASTE FORM. Ahmad Gabr Solomah, Engineering Research Services Division, North Carolina State University, Raleigh, NC 27650.

The effects of γ-irradiation on the chemical stability and particularly, the leaching behavior of sintered Modified SYNROC-B ceramic waste form[1] loaded with 10 wt % simulated high level radioactive waste (PW-4b) have been investigated. Using a Co^{60} as a gamma irradiation source, leaching experiments have been conducted according to the Materials Characterization Center Leach Test procedures and requirements (MCC-1) at the ambient temperature and pressure (25°C and 1 atmosphere). Deionized water was the leachant medium. Similar leaching experiments have been carried out in the absence of γ-irradiation and the leach rates of U, Ce and Fe are presented for comparison studies. Acid/Base formation has been monitored through pH measurements of the solution. Figure 1 shows the effects of γ-irradiation on the leaching behavior of sintered Modified SYNROC-B ceramic waste form by indicating the leach rates of Fe^{+2} and Ce^{+3} as a function of the leaching time (i.e., the accumulated radiation dose). Data from leaching experiments for longer periods (up to 6 months) are available for other high level radioactive waste constituents (e.g., U).

[1] A.G. Solomah, T.M. Hare and H. Palmour, III, Trans. Am. Nuc. Soc. 34, 197 (1980).

H17 MIGRATION OF RADIONUCLIDE CHAINS IN SUBSEABED DISPOSAL; A. K. Ray; Department of Chemical Engineering; University of Kentucky; Lexington, KY 40506, and H. E. Nuttall; Department of Chemical and Nuclear Engineering; University of New Mexico; Albuquerque, NM 87131.

The two dimensional (r-z) migration of radionuclides released from a canister located in a sedimentary layer bounded at the top by the ocean and at the bottom by an impermeable basalt zone is analyzed to determine the transport rates of radionuclides to the ocean floor. The radionuclide in the canister is assumed to decay in the following chain form

$$A_1 \xrightarrow{\lambda 1} A_2 \xrightarrow{\lambda 2} A_3 \xrightarrow{\lambda 3}$$

Analytical solutions were obtained for the concentration distributions, for the flux at the sediment/ocean interface and for the discharge rate to the ocean floor for each chain member. Using the properties of chain members present in actinide decay systems, the effects of canister placement depth, half-life, adsorption equilibrium and other relevant parameters are elucidated.

H18 STANDARD TESTS FOR THERMAL STABILITY OF NUCLEAR WASTE FORMS*, W. J. Gray, R. P. May and W. J. Weber. Pacific Northwest Laboratory, Richland, WA 99352.

Three standard tests for evaluating the thermal stability of nuclear waste forms have been proposed by the Materials Characterization Center (MCC). The effects of thermally-activated phase transformations on the properties of nuclear waste forms are measured by the MCC-7 Thermal Phase Stability Test. The MCC-8 High Temperature Vaporization Test measures the vaporization of fission products and other condensable elements from nuclear waste forms at high temperatures. The potential pressurization of a canister at elevated temperatures is determined by the MCC-9 Thermal Gas Generation Test which measures pressure of noncondensable gases from various waste forms as a function of temperature. The three tests will be described in detail and results for several waste forms will be presented.

* This work was performed for the Department of Energy under Contract DE-AC06-76RLO 1830.

9 RADIATION EFFECTS IN RADWASTE GLASSES: A REAPPRAISAL OF ALPHA-RECOIL AGING AS SIMULATED BY ION IMPLANTATION, J. C. Dran, Y. Langevin, M. Maurette, J. C. Petit, Laboratoire Reni BERNAS, 91406 ORSAY, FRANCE.

In order to investigate the radiation effects due to the recoil nuclei emitted during the alpha-decay of actinides in HLW glasses, we have developed an experimental procedure based on an external implantation of 1 keV/a m u lead ions coupled with leach tests in simulated natural waters and profilimetric measurements with a stylus instrument, which reveals irradiation effects as step heights between irradiated and non-irradiated areas. Our main result was the observation of a threshold effect on the chemical reactivity of glass above a critical ion dose, $phi_c \sim 5.10^{12}$ ions . cm^{-2}, equivalent to an internal dose of $\sim 2.10^{18}$ alpha-recoils . g^{-1}. The relevance of this approach was questionable, mainly because such a radiation effect has never been previously observed by using doping techniques and thus has been attributed to various possible ion implantation artefacts.

In this paper, we present new data on the irradiation of glasses and insulating minerals with a wider range of fluences than previously used (from 10^8 to 10^{16} $Pb.cm^{-2}$), which show that this reported threshold effect is well accounted for by a model of alpha-recoil registration in insulators.

20 RHEOLOGICAL CHARACTERIZATION OF CEMENTITIOUS GROUTS USED TO DISPOSE OF INTERMEDIATE - LEVEL RADIOACTIVE WASTE BY HYDROFRACTURING AT OAK RIDGE NATIONAL LABORATORY, E. W. McDaniel and J. G. Moore, Chemical Technology Division, Oak Ridge National Laboratory, P. O. Box Y, Oak Ridge, TN 37830.

The hydrofracturing process is a waste disposal process in use at the Oak Ridge National Laboratory for the permanent disposal of locally generated waste solutions. This process is now being modified to use in the disposal of sludge that result from the sodium hydroxide neutralization of acid waste solutions. In this process, the sludges will be slurried in a bentonite clay suspension and mixed with a solids blend of cement and other additives. The amount of dry solids required for each liter of waste slurry will be determined from a rheogram that relates the viscosity of the slurry with the grams/liter recommended for grouts with desirable flow properties.

A description of the process and the development of rheograms are included. Data are presented on the use of chemical additives to control the flow properties of grouts.

11 ENHANCED DISSOLUTION OF GLASS IN THE PRESENCE OF SALTS AND RADIATION DAMAGE*. C. Burman and W.A. Lanford+, Physics Department and Particle Solid Interaction Institute, State University of New York at Albany, Albany, N.Y. 12222.

Rutherford backscattering spectrometry and nuclear reaction analysis are used to study the reaction between aqueous solutions and glass. These techniques provide very sensitive methods to study the hydrogen incorporation, selective leaching and dissolution which result from the exposure of glass to aqueous solutions. The methods will be described as will their application to the study of the effects of salts and radiation damage on the reaction between water based solutions and glass. It is found that the presence of salt increases the dissolution rate of soda-lime glass several orders of magnitude over that in distilled water. The effects of prior radiation damage caused by 1 MeV Xe ions on dissolution and ion exchange rates will be discussed.

*Research sponsored in part by a grant from the Office of Naval Research.
+Alfred P. Sloan Foundation Fellow.

12 INFLUENCE OF GLASS COMPOSITON AND ENVIRONMENTAL PARAMETERS ON THE DURABILITY OF ALPHA-RECOIL-AGED RADWASTE GLASSES, J. C. Dran, M. Maurette, J. C. Petit, B. Vassent, Laboratoire Rene BERNAS, 91406 ORSAY (FRANCE).

The ion implantation simulation that we have developed in order to investigate the possible radiation effects associated with the alpha-decay of actinides (alpha-recoil aging) on the leachability of HLW glasses (1) presents the major advantage of allowing the detailed study of a very great variety of parameters susceptible to affect the long terme release of radionuclides. In this paper, we have particularly focussed our attention on the influence of glass composition and environmental parameters (T, P, pH, salinity, composition of the leaching solutions, etc. . .) on the leach rates of glasses irradiated above the critical dose $phi_c \sim 5.10^{12}$ Pb ions cm^{-2}.

In order to investigate the specific effect of each of the major environmental parameters on the leachability of irradiated glass, we performed a series of experiments on a limited sampling of glass compositions (soda-lime and two borosilicates) irradiated with a Pb fluence exceeding phi_c.

13 VALENCE STATE DETERMINATION AND THE EFFECT OF RADIATION ON LEACHING OF BOROSILICATE GLASS. D. P. Karim, D. J. Lam, K. L. Nash, A. M. Friedman, J. C. Sullivan, and S. Fried, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439.

Oxides of Np and Pu have been dissolved in a multicomponent borosilicate glass and examined using x-ray photoemission spectroscopy. Chemical shifts of the actinide 4f binding energies showed the concurrent presence of two separate Pu oxidation states in approximately equal abundance in an air melted sample. A similarly prepared Np glass, in contrast, showed relatively narrow 4f lines indicating a single predominant oxidation state. The Ti $2p_{3/2}$ core level (at $\sim$459 eV) is a convenient reference line from which accurate relative binding energies may be determined. The valence band spectra of these glasses exhibit low binding energy features which can be identified as due to occupied actinide levels.

Samples of 76-101 glass prepared with two percent PuO_2 were leached for varying lengths of time in the presence and absence of one megarad/hour gamma radiation field. The leachates and the glass surface were analyzed for plutonium by radiochemical procedures and by x-ray photoelectron spectroscopy, respectively.

Analysis of the leachates indicated significantly higher levels of plutonium in solution which contacted the irradiated samples. At least 50 percent of this plutonium occurs in the higher oxidation states [Pu(V) and Pu(VI)] despite being predominantly Pu(IV) in the glass. X-ray photoelectron spectroscopic analysis of the surface of unleached, leached, and leached in a radiation field, glasses support the results of the leachate analysis.

*Work performed under the auspices of the United States Department of Energy, Office of Basic Energy Sciences under contract number W-31-109-ENG-38.

14 ION IMPLANTATION STUDIES OF NUCLEAR WASTE FORMS,* C. J. Northrup, G. W. Arnold and T. J. Headley, Sandia National Laboratories,** Albuquerque, New Mexico, 87185.

A new and fundamental study of the radiation effects in nuclear waste forms (Sandia titanate ceramics and PNL-76-68 borosilicate glass) will be described. This study concentrates on those processes associated with the structural damage due to the recoil nucleus resulting from alpha decay. The damage along the recoil nucleus track was investigated by irradiating simulated waste forms with lead ions to depths equal to or less than 800 angstroms. The samples of Sandia titanate waste forms were then analyzed with a number of techniques such as Scanning Transmission Electron Microscopy, Rutherford Backscattering, and Elastic Recoil Detection. After irradiation the titanate waste form displayed defect clusters typical of alpha radiation damage in crystalline solids. Short term leach tests are being performed on the irradiated zirconolite, rutile, perovskite, and hollandite phases. Comparable irradiations of the PNL-76-68 borosilicate glass suggest compositional and structural changes occur along the damage track. The compositional changes can occur through interdiffusion of near-surface atoms of hydrogen and the alkali and alkaline earths in the damage zone. Effects of subsequent leaching of the irradiated glasses are also being determined.

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** A U. S. Department of Energy facility.

15 EFFECT OF ALPHA, GAMMA, AND ALPHA-RECOIL RADIATION ON BOROSILICATE GLASS CONTAINING DEFENSE HIGH-LEVEL NUCLEAR WASTE.* Ned E. Bibler, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC 29808.

At the Savannah River Plant, the proposed reference process for the preparation of defense high-level waste (DHLW) for geologic storage is the immobilization of the waste into borosilicate glass. During geologic storage (10^6y), the glass will be exposed to ~3 x 10^{10} rad of β radiation, ~10^{10} rad of γ radiation, and 10^{18} particles/g glass for both α and α-recoil radiation. This paper discusses tests of the effect of these radiations on the leachability and density of the glass. For these tests, glass containing simulated DHLW was prepared with frit of the current composition in the reference process. Three methods were used to irradiate the glass: external irradiations with beams of ~200 keV Xe or Pb ions, internal irradiations with ^{244}Cm-doped glass, and external irradiations with ^{60}Co γ rays. Results with both Xe and Pb ions indicate that a dose of 3 x 10^{13} ions/cm^2 (simulating >10^6 years storage) does not significantly increase the leachability of the glass in deionized water. Results with brines will also be discussed. Tests with ^{244}Cm-doped glass show no increase in leach rate up to a dose of 9 x 10^{17} α and α-recoils/g glass. Results of larger doses will be presented. The density of the ^{244}Cm-doped glass has decreased by 1% at a dose of 9 x 10^7 particles/g glass. With γ radiation, the density has changed by <0.02% at a dose of 6 x 10^{10} rad. Results of leach tests with γ-irradiated glass will also be discussed.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

16 PROPERTIES OF ALPHA-DOPED GLASSES REFERRING TO THE LONG TERM DISPOSAL OF SOLIDIFIED HIGH LEVEL RADIOACTIVE WASTES, N. Jacquet-Francillon and E. Vernaz, The French Atomic Energy Commission.

Research concerning samples of actinide doped glasses begun at an earlier date has been continued. The quantity of helium diffused and occluded on one hand and the quantity theoretically formed on the other have agreed.

No significant variation of the leaching rate of the CM 244 sample was noted after 450 days of leaching. It is to be remarked that during this period the cumulated alpha dose rose from 1.8.10^{18} to 2.5.10^{18} disintegrations/g. The stability of the alpha leaching rate between 25°, 50° and 70° which had already been demonstrated using Pu 238 doped glass has been confirmed using an AM 241 doped glass. The PH of the leaching solution rises little with the temperature. Finally, several preliminary studies concerning the effect of the ratio SA/V on the leaching rate of a sample of AM 241 doped glass seem to indicate that the leaching rate decreases when this ratio increases.

The majority of the leached alpha activity is trapped in an 8 mu filter. There is always, however, a small proportion of the activity which is not trapped by the ultri-filtering (<250 A). These results stand for all the PU, AM and CM samples. Leaching at 50 to 70° of Pu and AM samples indicate that when the temperature is increased, the fraction of course activity is also increased to the detriment of fine activity.

No variations of the microhardness or density due to the time factor have been observed.

In conclusion, the tests carried out up to date to not demonstrate any harmful effects of alpha activity in borosilicated glasses.

17 STUDY OF THE METAMICT TRANSFORMATION IN α-QUARTZ USING HIGH-RESOLUTION LATTICE IMAGING AND CONVERGENT BEAM ELECTRON DIFFRACTION. M. R. Pascucci, Department of Metallurgy and Materials Science, Case Western Reserve University, Cleveland, OH 44106, J. L. Hutchison, Department of Metallurgy and Science of Materials, Oxford University, Oxford OX1 3PH, U.K., S. McKernan and J. A. Eades, H. H. Wills Physics Laboratory, Bristol University, Bristol BS8 1TL, U.K. and L. W. Hobbs, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

A potential difficulty in the use of crystalline waste forms for solidification of nuclear wastes is their transformation to the metamict state in the waste irradiation field. This transformation is known to afflict both silicate wasteforms and the zirconolite phase of SYNROC. While the metamict state appears X-ray amorphous and involves a large specific volume increase, it nevertheless differs from conventional glassy states, although the details of its structure are equally difficult to elicit, *e.g.* by diffraction techniques. We have addressed this solid-state transformation, both experimentally and theoretically within the framework of topological models advanced for glass formation, in order to better characterize the metamict state through the details of how it is formed. We have chosen to study the metamict transformation in α-quartz and have employed two high-resolution electron microscope techniques: direct structure imaging (SI) and convergent beam electron diffraction (CBD). Evidence from both SI and CBD in α-quartz undergoing metamictization by radiolysis in the electron beam argue for a transformation model in which progressive disorder evolves from small displacement of individual [SiO_4] coordination units, made possible by lowered connectivity, within a framework of long-range correlated material.

I8 RADIATION EFFECTS IN NUCLEAR WASTE GLASSES - D. G. Howitt, J. F. DeNatale, D. K. McElfresh; Department of Mechanical Engineering; University of California; Davis, California 95616

The role of radiation damage to the stability of nuclear waste composites is twofold, radiation damage to the material itself and to the environment surrounding it. In the event that the surrounding environment is air saturated water the radiolytic products formed, notably nitric acid, can have a significant effect on the leach rates as can the more predictable effects of radiation damage to the physical structure of the composite. The direct observation of these effects by in-situ transmission electron microscopy methods will be described and discussed.

I9 INFLUENCE OF IRRADIATION WITH GAMMA-QUANTA AND BEAM OF ACCELERATED ELECTRONS ON THE SORPTION PARAMETERS OF CLAY MINERALS OF THE MONTMORILLONITE GROUP, V. I. Spitsyn, V. D. Balukova, M. K. Savushkina, Academy of Sciences, USSR.

Three minerals belonging to the montmorillonite group were studied. They are pyrophyllite, montmorillonite and nontronite. These minerals differ in the isomorphism degree and, consequently, in the charge of the elementary layer. Irradiation was performed at the Co^{60} installation (dose rate 13 mrad/hour, absorbed doses $10^8 - 10^{10}$ rad) and at the linear accelerator with the electron energy 1 MeV (dose rate $3 \cdot 10^7$ rad/hour, absorbed doses $10^7 - 10^8$ rad).

Under irradiation were air-dry minerals as well as those in solutions containing ^{90}Sr, which gave us an opportunity to study the irradiation influence on the sorption accumulation of radionuclides. Structural changes in the minerals were determined by the difractometric method.

The analysis of the difractograms of irradiated and nonirradiated minerals shows that the structure of the minerals belonging to the montmorillonite group remains unchanged, while alumosilicate layers converge which results in a decrease in interplane distances.

I10 MICROSTRUCTURAL STABILITY OF WASTE GLASSES UNDER IRRADIATION M. Antonini *, A. Manara, Joint Research Centre, 21020 Ispra (Varese) Italy and S.N. Buckley, Atomic Energy Research Establishment, OX 11 ORA, Harwell, England

The radiation stability of pure silica, borosilicate glasses and of glasses containing simulating waste oxides has been investigated by means of optical spectroscopy and high voltage electron microscopy. Pure silica samples have been irradiated with Ni^{+6} ions at an energy of 46.5 MeV and protons of 1 MeV. The optical absorption spectra of the irradiated samples have been recorded in the range 4 to 8 eV. The decrease of the observed peaks following thermal annealing of the damage indicates that a large fraction of the defects produced just after irradiation are electronic modifications of pre-existing "precursor" defects. Borosilicate samples and glasses containing waste simulating oxides have been electron irradiated and examined "in situ" by transmission electron microscopy. Large gas bubbles are observed at dose rates exceeding 10^{22} e/m^2.

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J1 RUTHERFORD BACKSCATTERING INVESTIGATION OF THE LEACHING CHARACTERISTICS OF BOROSILICATE GLASS.* L. A. Boatner, H. Naramoto, C. W. White, and B. C. Sales, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830.

The technique of Rutherford backscattering (RBS) has been used to monitor leaching-induced changes in the chemical composition of the 1-2 micron surface layer of borosilicate glass. A borosilicate glass with the composition: 50 wt. % SiO_2, 21 wt. % B_2O_3, 20 wt. % Na_2O and 4 wt. % MgO was doped with 5 wt. % $^{238}UO_2$. The RBS depth-profile spectrum of a polished unleached glass specimen indicated that the ^{238}U concentration was uniform throughout the 1-2 micron surface region probed by means of this technique. After leaching the identical sample in distilled water at 90°C for 11, 22 and 44 h, all three RBS depth-profile spectra revealed a dramatic increase ($\sim$ 300%) in the ^{238}U concentration within 150 Å of the surface. Additional RBS depth-profile data will be presented on the leaching characteristics of Sr, Cs, Fe and other elements in material made using type 21, type 131, and related borosilicate glass compositions. The present results show that depth profiling by Rutherford backscattering can be a powerful, nondestructive technique for investigating the effects of various environmental conditions on the surface properties of nuclear waste glasses.

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J2 DEVELOPMENT OF SPHENE-BASED GLASS CERAMICS TAILORED FOR CANADIAN WASTE DISPOSAL CONDITIONS. Peter J. Hayward and E.V. Cecchetto, Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada, ROE 1LO.

Glass ceramics and ceramics based on minerals of proven thermodynamic stability in Canadian Shield groundwaters are being developed to host possible future CANDU recycle wastes. Sphene-based glass ceramics, produced by reheating phase-separated Na_2O-Al_2O_3-CaO-TiO_2-SiO_2 glasses to approximately 1000°C, show strong partitioning of waste ions into the sphene ($CaTiSiO_5$) lattice. Leaching results suggest that these materials are extremely durable in deionised water: in simulated groundwaters, the sphene phase appears to suffer no net leaching. Leach testing, manufacturing methods and alternative preparative routes are discussed.

J3 THE DEVELOPMENT AND TESTING OF SYNROC C AS A HIGH LEVEL WASTE FORM. K.D. Reeve, E.J. Ramm, D.M. Levins, J.L. Woolfrey and W.J. Buykx, AAEC Research Establishment, Private Mail Bag, Sutherland, NSW 2232, Australia.

The fabrication of SYNROC C containing inactive simulated waste is being demonstrated by the method of in-can hot pressing. This involves the use of a laterally supported closed-end stainless steel tube as the hot pressing die. The equipment forms part of a demonstration line designed to produce 10 cm diameter by 90 cm long blocks of SYNROC fully canned in stainless steel.

Other aspects of the AAEC's SYNROC development program include leach testing of SYNROC C according to modified IAEA and MCC-1 procedures; the simulation of actinide decay damage in SYNROC B, SYNROC C, barium hollandite, perovskite and zirconolite using fast neutrons; and the measurement of thermal diffusivity, specific heat and thermal conductivity of the same five materials over the temperature range 25-700°C.

J4 THE LEACHING BEHAVIOUR OF THE SWEDISH KBS-GLASSES ABS-39 AND ABS-41, Hans-Peter Hermansson and Hilbert Christensen, The Royal Institute of Technology, S-100 44 Stockholm, Sweden.

The Swedish KBS glass corrosion investigation program is focused on two compositions known as ABS-39 and ABS-41. Both are borosilicate glasses with a fission product content of 9% and a general composition which should prove to be very close to the final cogema compositon.

These glass qualities containing simulated fission products have been leached using a procedure similar to the PNL MCC-1 test procedure. The test matrix has comprised three temperatures (i.e., 25, 40 and 90°C) and exposure times of 1, 3, 7, 14, 28, 91 and 182 days.

Eight types of leachants have been used, namely, distilled water, carbonate and silica water, and brine, and four more complex waters to simulate different groun waters.

The leachates hae been subjected to elementary analysis. The glass specimens have been checked for weight losses and investigated with IRRS.

J5 COMPARATIVE IMPACT PROPERTIES OF FIVE SOLID ALTERNATIVE SAVANNAH RIVER LABORATORY DEFENSE HIGH-LEVEL WASTE FORMS. L.J. Jardine, G.T. Reedy, and W.J. Mecham, Argonne National Laboratory, Argonne, IL 60439.

Impact test data of solid waste forms will be used in conjunction with other characterization properties to assess the performance of waste forms during handling, transportation, storage and repository conditions. The particle size distribution of fragments, including the quantity of particles which could become airborne or respirable, is one measureable test response of major interest for future risk analyses.

A series of uniform comparative drop weight MCC-10 type impact tests were conducted on five alternative waste forms under consideration for immobilizing Savannah River Laboratory (SRL) defense wastes. The fragment size distributions were measured in the size ranges of 4 to 8000 μm.

All waste form fragments were described by lognormal size distributions. The quantities of respirable sizes (i.e., arbitrarily defined in this comparative study as <10 μm diameters) were determined from the lognormal size distributions. The borosilicate glass and SYNROC specimens yielded the same fractions of respirable sizes; the FUETAP concrete and the high silica glass yielded ~2-3 times more respirable sizes than the borosilicate glass or SYNROC while the tailored (Spinel) ceramic yielded about half as much respirable sizes as the borosilicate glass and SYNROC. Correlations of these observations with waste form properties are being investigated and modeled to provide the data base needed to apply these laboratory scale tests to realistic full scale waste forms.

J6 A METHODOLOGY FOR CHARACTERIZING BRITTLE FRACTURE OF SOLID WASTE FORMS FROM ACCIDENTAL IMPACTS. W.J. Mecham, L.J. Jardine, and M.J. Steindler, Argonne National Laboratory, Argonne, IL 60439.

A general method for characterizing the major practical effects of accidental impacts on waste packages and for evaluation of scale-model tests has been developed. Impact fracture of brittle waste forms has been shown to produce particulates whose size distributions are described by the lognormal probability distribution. The process model proposed for fragment generation involves the transformation of impact (kinetic) energy into elastic strain energy which is followed by fracture and energy dissipation into heat by the fracture particulates. The peak stresses developing during energy absorption during compressions are approximated as a function of time using elastic theory for a wide range of practical impact conditions for typical (glass) waste forms. The proposed methodology requires experimental validation in terms of correlation of energy dissipated with the volume integral of elastic energy created during the initial stages preceding fracture, with the resulting particulate surface area, and with the lognormal parameters.

J7 ALKOXIDE DERIVED AMORPHOUS SOLIDS AS AN ALTERNATE NUCLEAR WASTE FORM. J. M. Pope and D. E. Harrison, Westinghouse Research and Development Center, 1310 Beulah Road, Pittsburgh, PA 15235.

Liquid nitrate acid waste can be immobilized in an amorphous aluminosilicate matrix that is produced by polymerization of metal alkoxides. Unlike vitreous aluminosilicate host matrices, neither alkalies, alkaline earths, nor borates are required since no melting is involved. Rather, chemical polymerization of aluminum and silicon alkoxides and waste metal nitrates results in gelation of the waste composition at room temperature. Heating this gel to 500°C removes residual alkyls and water and causes a ninety percent volume reduction. Because of the magnitude of this shrinkage, the dried gel is comminuted into ~5 mm size granules. After calcining at 500°C, these amorphous granules have an apparent surface area of ~300 m^2/g; heating them to 850°C decreases the surface area to ~1 m^2/g. The static leach rate measured in deionized water at 90°C for both porous and dense granules is comparable to vitreous aluminosilicate waste forms of similar composition, when adjustment is made for the apparent high surface area of the amorphous granules. This result suggests that the leach rate of the granules is at least as low as vitreous aluminosilicate waste forms that have been prepared at 1300°C.

Another outstanding property of the amorphous granules is the high waste loadings that are possible in comparison to vitreous waste forms (up to 50%).

High irradiation fields appear to have no adverse effect on the polymerization process. A cobalt-60 source placed in direct contact with the alkoxide-waste solution for 24 hours to give a fluence of 10^7 R had no detectable effect on the gelation process.

Neither did beta radiation to a fluence of 10^7 R as produced by a van de Graaff generator operating at a beam current of 100 mu amp and a beam voltage of 2 MeV to give 200 watts self-heating in the solution. Subsequent physical and chemical characterization of the "irradiated" product showed it to be indistinguishable from the unirradiated material.