UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Gaithersburg, Maryland 20899

February 17, 1988

Mr. Charles Peterson
Technical Review Branch
Division of High-Level Waste Management
Office of Nuclear Materials Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555

Re: Monthly Letter Status Report for January 1988 (FIN-A-4171-7)

Dear Mr. Peterson:

Enclosed is the January 1988 monthly progress report for the project "Evaluation and Compilation of DOE Waste Package Test Data" (FIN-A-4171-7). The financial information is reported separately.

Sincerely,

Charles G. Interrante

Charles G. Interrante
Program Manager
Corrosion Group
Metallurgy Division

Enclosure

Distribution:
NMSS PM (1)
Ofc of the Director
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Monthly Letter Report for January 1988

Published February 1988

(FIN-A-4171-7)

Performing Organization: National Bureau of Standards (NBS)
Gaithersburg, MD 20899

Sponsor: Nuclear Regulatory Commission (NRC)
Office of Nuclear Materials Safety and Safeguards
Washington, DC 20555

Task 1 -- Review of Waste Package Data Base

The NBS/NRC database is being converted to a more powerful and faster database management system (DBMS). It is called Advanced Revelation. For this conversion, eight working (data-containing) files will be ported to the new DBMS; the dictionaries corresponding to these files must be ported, and any programs within the dictionaries must be recompiled. Routines used for entering data into the system are called data entry windows and these must also be restructured. Four data entry files used in this database (work.abs, work.ref, work.fig, work.key) and their corresponding dictionaries were converted to the Advanced Revelation format in January. New windows are now being developed to permit the display of information pertinent to each of these four files. While work continues on this conversion process, the DBMS called Revelation will be maintained in a fully operational status for use by NBS and NRC users.

STATUS OF REVIEWS ON OTHER RELATED REPORTS

Appended to this report are the following three Draft Reviews not previously submitted. Each of these reports concerns tests conducted to assess environmental sensitivities of materials that had been proposed for use by the Basalt Waste Isolation Project (BWIP). These tests, for assessment of environmental sensitivities of materials, are pertinent to our current work, on waste package performance for the Yucca Mountain site, which is conducted under the Nevada Nuclear Waste Storage Investigations (NNWSI) reports, studies and plans. The data is expected to be useful as reference material for future reviews of NNWSI work. As we have discontinued work related specifically to BWIP, each of these reviews is presented as a non-critical review.

1. SD-BWI-TS-012, "Short-term Stress-Corrosion-Cracking Tests for A36 and A387-9 Steels in Simulated Hanford Groundwater," January 1985.

2. SD-BWI-TI-165, "Technical Progress Report on BWIP Canister Materials Crack Growth Study for FY 1983," January 1984.

3. RHO-BW-SA-560P, "Status of Environmentally Assisted Cracking Studies by the Basalt Waste Isolation Project," Symposium on Radioactive Waste Management '86, March 1986.

STATUS OF REVIEWS OF NNWSI REPORTS

Five reports were identified for review on Nevada Nuclear Waste Storage Investigations (NNWSI) during this month. One on the subject of materials for the metal canister, three dealing with materials in the container, and one dealing with the container environment.

The report on canister materials (McCright, 1987) summarizes the results of a five-year study on three austenitic alloys and three copper-based materials. Uniform/pitting corrosion is observed, but is not considered a serious problem for any of the materials. Furthermore, transgranular stress-corrosion cracking is observed on some of the austenitic alloys under some conditions of exposure.

Dissolution tests, using distilled and J-13 water, have been carried out on bare and clad spent-fuel samples where the cladding was defected (Wilson, 1985). Preliminary results indicate that slit defected cladding exhibited more release than specimens with smaller laser-drilled holes through the cladding, and bare fuel exhibited more release than either slit or hole-defected specimens. Preliminary results on the effect of microstructure on the leaching rate of spent fuel show that irradiated, friable spent fuel has a much higher leach rate than the unirradiated material. Greater release rates of Cs and Tc were observed for the fuel of finer grain size, when compared with that for the coarser grained fuel.

A plan designed to determine the rate of release of radionuclides from breached containers for glass waste is described (Aines, 1987). The ultimate goal of the plan is to provide input to the waste-package performance- assessment model in the form of data from the radionuclide release model.

This report describes the results of a study on the influence of copper on degrdation of zircaloy spent-fuel cladding (Smith, 1987). The results indicate that after five months of exposure under the conditions of this simulated tuff repository environment, corrosion is not significant. The conditions in which copper has been observed to induce zircaloy corrosion are different from the potential tuff repository conditions.

A study on the reaction of simulated tuff ground water with glassy tuff shows the formation of zeolites as predicted by geochemical modeling calculations (Knauss and Peifer, 1986). This agreement with the predictions was observed to extend over a range of temperatures from 90 to 250°F at elevated pressure.

NNWSI -- Reports identified and assigned for review this month.

1. Aines, R. D., "Plan For Glass Waste Form Testing For NNWSI", UCID-21190, September 1987.

2. Knauss, K. G., "Reaction of Vitric Topopah Spring Tuff and J-13 Ground Water under Hydrothermal Conditions Using Dickson-Type, Gold-Bag Rocking Autoclaves", UC RL-53795, November 1986.

3. McCright, Halsey, S. G., Konynenburg, R. A., "Progress Report on the Results of Testing Advanced Conceptual Design Metal Barriier Materials Under Rilevant Environmental Conditions for a Tuff Repository", UCID-21044, December 1987.

4. Smith, H. D. , "The Influence of Copper on Zircaloy Spent Fuel Cladding Degradation Under a Potential Tuff Repository Condition", UCRL-15993, SANL-622024, March 1987.

5. Wilson, C. N., "Microstrctural Characteristics of PWR Spent Fuel Relative to its Leaching Behavior", UCRL-15976, SANL-522-006, April 1985.

NNWSI -- Review is continuing on the following 16 reports.

1. UCRL-94708, "Carbon-14 in Waste Packages for Spent Fuel in a Tuff Repository," October 1986.

2. UCRL-94633, "Experimental Study of the Dissolution Spent Fuel at 85°C in Natural Groundwater," December 1986.

3. UCRL-95962, "Hydrogen Speciation in Hydrated Layers on Nuclear Waste Glass," January 1987.

4. UCRL-94658, "Integrated Testing of the SRL-165 Glass Waste Form," December 1986.

5. UCRL-91258, "Leaching Savannah River Plant Nuclear Waste Glass in a Saturated Tuff Environment," November 1984.

6. UCRL-92891,"LWR Spent Fuel Characteristics Relevant to Performance as a Wasteform in a Potential Tuff Repository," June 1985.

7. ANL-84-81, "NNWSI Phase II Materials Interaction Test Procedures and Preliminary Results," January 1985.

8. HEDL-TME 85-22, "Results from Cycles 1 and 2 of NNWSI Series 2 Spent Fuel Dissolution Tests," May 1987.

9. UCRL-94363, "Hydrological Properties of Topopah Spring Tuff - Laboratory Measurements," December 1985.

10. UCRL-53761, "Waste Package Performance Assessment: Deterministic System Model Program Scope and Specification," October 1986.

11. HEDL-7540, "Technical Test Description of Activities to Determine the Potential for Spent Fuel Oxidation in a Tuff Repository," June 1985.

12. HEDL-SA-3627, "Predicting Spent Fuel Oxidation States in a Tuff Repository," April 1987.

13. UCRL-53702, "Spent Fuel Test - Climax: An Evaluation of the Technical Feasibility of Geologic Storage of Spent Nuclear Fuel in Granite," March 1986.

14. UCRL-53767, "Geomechanics of the Spent Fuel Test - Climax," July 1987.

15. UCRL-92311, "Gamma Radiation Effects on Corrosion, I. Electrochemical Mechanisms for the Aqueous Corrosion Process of Austenitic Stainless Steels," February 1985.

16. UCID-20895, "Application of EQ3/6 to Modeling of Nuclear Waste Glass Behavior in a Tuff Repository," May 1986.

WASTE FORM DEGRADATION

Review of Chapter 4, "Dissolution of Specific Radionuclides," may be completed by the end of February. Chapter 2, "Surface Layers in Leached Borosilicate Glass High-Level Defense Nuclear Waste Forms," and Chapter 3, "Environmental Interaction," are expected to be completed within a month thereafter.

WASTE FORM DEGRADATION -- No new reports have been identified this month.

WASTE FORM DEGRADATION -- Review is continuing on the following 11 reports.

1. "Long Term Leach Behavior of West Valley HLW Glasses," P. B. Macedo, et al., ANS Spectrum, 1986.

2. "Leach Mechanisms of Borosilicate Glass Defense Waste Forms -- Effects of Composition," A. Barkatt, et al., Waste Management '86: Waste Isolation in the U.S.-Technical Programs and Public Education, March 1986.

3. "Chemical Determination of West Valley Waste Form Products," D. M. Oldman, J. R. Stimmel, and J. H. Marlow, March 1987.

4. "Method for Showing Compliance with High-Level Waste Acceptance Specifications," Waste Management '86: Waste Isolation in the U.S. Technical Programs and Public Education, Volume 2, High-Level Waste, March 1986.

5. PNL-5157, "Final Report of the Defense High-Level Waste Leaching Mechanisms Program," August 1984.

6. "Physical Chemistry of Glass Surfaces," J. Non-Cryst. Solids, 1978.

7. DP-MS-83-135, "Process Technology for Vitrification of Defense High-Level Waste at the Savannah River Plant," Paper for presentation in the proceedings of the American Nuclear Society Meeting on Fuel Reprocessing and Waste Management, August 1984.

8. DP-MS-86-96, "Process and Mechanical Development for the Savannah River TRU Waste Facility," Paper proposed for presentation at the American Nuclear Society International Meeting, Spectrum '86, September 1986.

9. PNL-4382, "Materials Characterization Center's Workshop on Leaching Mechanisms of Nuclear Waste Forms," May 19-21, 1982.

10. "Large Scale Leach Testing of DWPF Canister Sections," Proceedings of the Materials Research Society Symposium, "Scientific Basis for Nuclear Waste Management X," December 1986.

11. "Waste Glass Leaching: Chemistry and Kinetics," Proceedings of the Materials Research Society Symposium, "Scientific Basis for Nuclear Waste Management X," December 1986.

TASK 2 -- Identification of Additional Data Required and Identification of Tests to Generate the Data

NBS lead workers are continuing their studies concerning the types of additional data and verification tests needed to demonstrate that the DOE waste package designs will meet the performance objectives of 10 CFR 60.

Conclusions, results, and recommendations for the work reviewed to date are given in each review form under the heading GENERAL COMMENTS OF REVIEWER.

TASK 3 -- Laboratory Testing

The work on each of the four projects reported below is on schedule with the work statements listed in their respective proposals. The work conducted in January 1988 is reported below. Work conducted in previous months was reported earlier.

Title of Study: Evaluation of Methods for Detection of Stress Corrosion Crack Propagation in Fracture Mechanics Samples.
Principal Investigator: Charles Interrante

In January, a relay actuator, which had been sent out for repair in December, was fixed and returned.

In addition, it was also determined that the calibration data taken at the end of December will have to be retaken. The software used to collect the calibration data will have to be modified to give a longer time delay statement whenever the polarity of the current is reversed. This extra delay between readings will give the meters enough time to settle sufficiently to give an accurate reading.

A live test of the acoustic-emission apparatus was initiated on January 23rd. The test used a specimen that had been wedge loaded at a stress-intensity of 30 ksi√in. Started at 10:48:53 hours, this test was stopped at 11:03:22 due to a broken lead connection. After the specimen was disassembled and repaired, the test was restarted, on January 24th at 18:00:00, but no acoustic events were detected for the next 24 hours. At 18:17:00 hours, two 40 db preamps were added to the system at a location just before the differential amplifier. The result of adding the preamps was the immediate detection of acoustic events. The performance of the existing amplification system is being evaluated. The experiment was stopped on January 29th at 14:30:00 hours. The color of the environment at the completion of the experiment was a cloudy white. This was an indication to the project leader that oxygen could have leaked into the environmental chamber. Oxygen will significantly reduce the severity of this environment, and hence, the cracking caused by hydrogen. The data generated from the experiment was then transferred to the NBS mainframe where it is being processed.

Title of Study: Effect of Resistivity and Transport on Corrosion of Waste Package Materials.
Principal Investigator: Edward Escalante

Measurements of the corrosion rate of steel in the different environments is proceeding very well. The data continue to indicate that corrosion in the liquid environment is greater than it is for the sand or agar environment, as expected. The more difficult task of measuring the transport properties of oxygen in these same environments is continuously being improved as we develop a better understanding of the processes involved. Recently published work by other laboratories describe other approachs to the measurement of diffusivity. The incorporation of these new ideas, along with our own expanding experience, is improving our understanding of the results being obtained in our laboratory. All measurements are proceeding according to plan.

Title of study: Corrosion Behavior of Zircaloy Nuclear Fuel Cladding
Principal Investigator: Anna C. Fraker

The purpose of this work is to characterize the corrosion behavior of Zircaloy in terms of passivity, breakdown of passivity and susceptibility to localized corrosion. A brief review of corrosion of Zircaloy has been conducted and is not quite ready for release for comments, so it will be transmitted in the February report of progress on this project. Experimental work on the corrosion of Zircaloy is continuing. Some of the tests performed to date are described below.

Anodic polarization measurements have been made on twenty-one specimens of Zr-2 and Zr-4 tested in J-13 water at 95°C. Earlier tests were conducted to develop baseline data on the passive region and to determine the breakdown potential. These data, taken from material not yet extruded into tubing, indicated a passive region with a breakdown potential of +0.8 volts vs. a saturated calomel electrode (S.C.E.). The Zircaloy upon immersion in 95°C J-13 water would have an initial electrode potential of -0.736 volts vs. S.C.E., and this would change, after a period of fifteen minutes in the J-13 water, to a more positive value of -0.522 volts vs. SCE, indicating the formation of a surface oxide film.

The last ten tests have been conducted on Zr-4 and Zr-2 cladding tubes received from Babcock and Wilcox and General Electric Co., respectively. The scatter for the values of the breakdown potential is greater for the manufactured tubing than it is for the bulk material. The Zr-4 specimen (inner side of tubing was cleaned with abrasive Al_2O_3 prior to testing and the breakdown potential was 0.3 volts vs. S.C.E. Other data show a breakdown potential for the inner Zr-4 tubing of 0.75 volts vs. S.C.E. The outer side of the Zr-4 tube was abrasively polished in the same manner, and the breakdown potential was 0.7 volts vs. S.C.E. These variations in breakdown potential are being studied and will be discussed in more detail in a future report.

Cyclic polarization measurements in 95°C J-13 water on the Zr-2, Zr-4, Zr-2 tubing, and Zr-4 tubing all show, in plots of current vs. applied electrode potential, a hysteresis of 1 to 2 orders of magnitude in the current; this indicates that the material does not repassivate on reversing the applied potential. It is possible that changing some parameters of the test, such as time at a given potential, will reduce the high current of the return portion of the curve. This hysteresis, if not accounted for, could mean that Zircaloy is subject to pitting in J-13 water. Additional testing and data analysis will be conducted before making this determination.

The oxide-coated Zr-2 tubing from General Electric has a more positive initial electrode potential of -0.438 volts vs. S.C.E. and after 15 minutes, a potential of -0.380 volts vs. S.C.E. Anodic polarization of this material in 95°C J-13 water showed the current to be in the same order of magnitude as that of the other materials with some erratic behavior. Some additional tests will be run on this material.

Continuing work on this project will involve corrosion testing of welded tubing materials, and additional tests to determine Zircaloy's susceptibility to pitting in J-13 water. Other work will include characterization of microstructures using light microscopy, scanning electron microscopy and energy dispersive x-ray analysis.

Title of study: Pitting Corrosion of Steel Used for Nuclear Waste Storage.
Principal Investigator: Anna C. Fraker

This work has been completed.

TASK 4 -- General Technical Assistance

NBS staff members who attended the annual Materials Research Society Symposium in Boston, MA were Mr. E. Escalante, Dr. H. Ondik, Dr. E. Plante, Dr. R. Ricker, and Ms. J. Ruspi. A combined trip report writtent by these NBS workers is attached to this report (see p 21).

Dr. C. Interrante attended the ASTM C26.07 Subcommittee Meeting in Albuquerque, New Mexico on January 25-27, 1988. His report on this meeting will be given in the February report.

NBS Review of Technical Reports on the High Level Waste Package for Nuclear Waste Storage

DATA SOURCE

(a) Organization Producing Report

Westinghouse Hanford Co. for Rockwell Hanford Operations.

(b) Author(s), Reference, Reference Availability

James, J. A., "Short-Term Stress-Corrosion-Cracking Tests for A36 and A387-9 Steels in Simulated Hanford Groundwater," SD-BWI-TS-012, June 1985.

DATE REVIEWED: 10/6/87; Revised 11/13/87

TYPE OF DATA

(1) Scope of the Report

Experimental laboratory data

(2) Failure Mode or Phenomenon Studied

Corrosion (stress cracking) SCC
Cracking (environmentally assisted) EAC
Both SCC and EAC are referred to in the report. SCC is generally defined as EAC that occurs under static loading, while the more general term EAC can apply to both static and cyclic loadings. Both terms are used in the report since both types of loadings are employed in the overall program.

MATERIALS/COMPONENTS

ASTM A36 steel plate
ASTM A387 Grade 9 steel plate

One-inch plate stock of a type or grade of material proposed for use in waste container vessels.

Three tables are included providing material identification, condition, chemical composition from vendors certification sheets, and mechanical properties. Composition (weight %) for A36 (Pohang heat Y45659): C = 0.15, Si = 0.20, Mn = 0.96, P = 0.023, S = 0.014, Cu = 0.02; for A387 (Armco heat 45862): C = 0.11, Si = 0.23, Mn = 0.59, P = 0.012, S = 0.013, Cr = 8.70, Mo = 0.9. From laboratory tests at 150 and 250°C for A36: 0.2% offset yield strength = 305.4 and 269.5 MPa, ultimate strength = 565.4 and 585.2 MPa, total elongation = 15.4 and 21.1 %, reduction in area = 57.1 and 59.1 %. From vendors certification sheets at 24°C for A36 and A387: 0.2% offset yield strength = 315.7 and 522.6 MPa, ultimate strength = 467.8 and 686.0 MPa, total elongation = 28.0 and 22.0 %, reduction in area = (not given for A36), 65.7 % for A387.

TEST CONDITIONS

(1) State of the Material being Tested

ASTM A36 is a hot-rolled plate.
ASTM A387 is a wrought steel. It was austenitized at 899°C (1650°F) for 60 minutes and furnace cooled; transformed at 704°C (1300°F) for 250 minutes and air-cooled. No subsequent tempering was performed.

(2) Specimen Preparation

Modified wedge-open-loading (MWOL) specimens were used [the proper term is bolt-loaded 1T, modified-compact specimens, $MC(W_b)$]. Two figures show the specimens and a table contains the dimensions. Specimens were cyclically precracked in air at room temperature on an MTS electrohydraulic testing machine using load as the control parameter. The fatigue precracks simulated relatively long cracks. Maximum levels of the stress-intensity factor (K) achieved during precracking are given in a table (they were always less than the initial test K-levels which were 30, 40, and 60 MPa x $m^{1/2}$). After precracking, the elastic compliance of each specimen was measured using the load cell of the MTS machine and a clip gage (MTS Model 632.01) seated in the knife edges that are machined into the front face of the specimen. A table in the report gives the precracking conditions. Specimens were loaded initially by using a wrench to torque the specimen loading bolt, while holding the specimen in a vise with the crack pointed downward, until the desired initial crack mouth opening displacement (CMOD) was obtained. Plastic tape was used to "dam" the areas of the notch and the crack and these areas were filled with simulated Hanford groundwater prior to loading the specimen.

(3) Environment of the Materials being tested

Precracked, compliance tested, and loaded specimens were immersed in a container of static groundwater (i.e., no flow except to maintain a preset level) and the tape dams were removed from the specimens. The six specimens for a given test were placed in a carrier (still immersed) which was then set in an autoclave of approximately 3.9 liter capacity. (The specimen carrier was designed so that ceramic material prevented metal contact, either specimen-to-specimen or specimen-to-autoclave.) The autoclave was partially filled with the simulated groundwater when the loaded specimens were inserted. Specimen crack tips were in contact with groundwater, essentially continuously, from the moment loads were applied until insertion into the autoclaves. Specimens were then surrounded by a mixture of 1000 grams of Cohassett Flow basalt (crushed to -1/2 + 1/4 average mesh size) and 333 grams of powdered bentonite. The autoclave was then filled with simulated Hanford groundwater and sealed and pressurized. Two tables in the report contain the water chemistry for the two complete (2000 hour) tests that were conducted. The autoclaves were operated in a "static" mode, that is, no flow of groundwater occurred through the autoclaves except at periodic intervals (about once a week) to ensure that they remained full. Test pressure was 100 atmospheres and the temperature was either 150°C or 250°C.

METHODS OF DATA COLLECTION/ANALYSIS

Autoclave exposure of precracked MC(W_b) specimens (1T), using LEFM analyses of tests designed to explore the crack growth threshold, K_{th}. After the exposure time, of from 24 to 2000 h, the autoclaves were cooled, depressurized, and unloaded. Specimens were then placed in a vise and unloaded while measuring the amount of deflection recovered on unloading. The load corresponding to the deflection was then measured on the MTS machine. Specimens were then immersed in liquid nitrogen (to embrittle them temporarily) and fractured in the MTS machine. The average post-test crack length was determined by measurement of one of the broken specimen halves. Eleven individual measurements were made on each specimen: measurements on each specimen surface plus nine measurements through the thickness of the specimen at increments of 2.54 mm. An average of the 11 measurements established the mean crack length. The 11-point average crack length is considered more accurate than an average of the surface crack lengths because of the slight curvature of the crack front (often called tunneling).

AMOUNT OF DATA

Data for one short-term (about 24 h) and two complete tests (2000 h) are included. There are three tables listing measured and calculated results. Table 8 is titled "Summary of Measured and Calculated Results for Test No. 1 (<24 h at 250-270°C)." Table 9 is titled "Summary of Measured and Calculated Results for Test No. 2 (2180 h at 150°C)." Table 10 is titled "Summary of Measured and Calculated Results for Test No. 3 (2000 h at 250°C)." Each table lists initial and final applied K-levels, initial and final loads, initial and final displacements, plastic and wedged crack mouth opening displacements (V), initial and final compliances, average initial surface crack lengths, predicted initial and final crack lengths, and average final crack length. The data are for three specimens each of the two steels. The data are plotted in six load-displacement diagrams. Figure 12 is titled "Load-displacement Diagram for A36 Steel Specimens in Test No. 1." Figure 13 is titled "Load-displacement Diagram for A387-9 Steel Specimens in Test No. 1." Figure 14 is titled "Load-displacement Diagram for A36 Steel Specimens in Test No. 2." Figure 15 is titled "Load-displacement Diagram for A387-9 Steel Specimens in Test No. 2." Figure 16 is titled "Load-displacement Diagram for A36 Steel Specimens in Test No. 3." Figure 17 is titled "Load-displacement Diagram for A387-9 Steel specimens in Test No. 3." The diagrams give the applied K versus V for each of the two steels, for each of the triplicate tests. The K values range from 0 to 60 MPa x $m^{1/2}$ and the V values range from 0 to 0.6 mm.

The data are discussed by the authors in terms of the kind of cracking and deformation, evidence of plasticity, wedging, etc., and the effect of the temperature of the tests.

UNCERTAINTIES IN DATA

The load-displacement diagrams for the 24-h test carry the note that P_f and C_f, the final values of load and compliance repectively, were not measured and, therefore, the plots are only approximate.

There is a caution about the reliability of the compliance testing because the final compliances were generally lower than the initial compliances. This difference is physically impossible unless crack extension occurs. The most likely cause would be an anomalous measurement due to the wedging action of corrosion products and/or mineral deposits. Post-test examination of fracture surfaces revealed extensive deposits over the entire crack surface. Composition and depth of the deposits were not determined. It was pointed out that the conclusion (based on measured values of final crack length, a_f, and compliance estimates of a_o) that some crack extension may have taken place in the A387 Grade 9 steel is tentative. The observed differences between initial and final values are only slightly larger than the errors associated with the compliance technique.

DEFICIENCIES/LIMITATIONS IN DATABASE

Because precracking and compliance testing were done in air at K- levels lower than the initial test K-levels, the first application of the actual test loads occurred in the presence of the groundwater environment. Therefore, any dislocation generation, plasticity, or creation of new crack-tip surfaces occurred in the presence of groundwater at ambient conditions.

Ideally, these effects due to loading of the specimen should be permitted to occur only at the temperatures and pressures of the test, but that is impossible, as specimen loading must be done prior to placement in the autoclave where temperature and pressure increases are applied.

Longer term tests are required. Although no cracking was observed in the A36 steel the results might be quite different in longer term tests. The apparent anomalous crack extension of the A387 steel must be clarified by further tests.

An extensive appendix discusses the factors influencing crack lengths calculated using compliance measurements on WOL MC(W_b)] specimens.

KEY WORDS

Experimental data, linear-elastic fracture mechanics (LEFM), laboratory, Hanford, simulated groundwater, basalt, bentonite, ambient temperature, high temperature, high pressure, static (no flow), stainless steel, carbon steel, ASTM A36, ASTM A387 Grade 9, annealed (austenitized and transformed), wrought, precracked, MC(W_b), 1T, crack extension, corrosion (stress cracking) SCC.

GENERAL COMMENTS OF REVIEWER

This is a non-critical review.

RELATED HLW REPORTS

SD-BWI-TI-120
SD-BWI-TI-165
RHO-BW-SA-560P

APPLICABILITY OF DATA TO LICENSING
Ranking: key data ( ), supporting data (X)

(a) Relationship to Waste Package Performance Issues Already Identified

This report relates to ISTP issue, 2.2.4, identification of potential corrostion failure modes. In this case, the possibility of the localized corrosion mode of stress corrosion cracking (SCC) was investigated at elevated temperatures and found to be inconclusive for A387-9 wrought steel.

(b) New Licensing Issues

(c) General Comments on Licensing

NBS Review of Technical Reports on the High Level Waste Package
for Nuclear Waste Storage

DATA SOURCE

(a) Organization Producing Report

Westinghouse Hanford Company for Rockwell Hanford Operations, Engineered Barriers Department.

(b) Author(s), Reference, Reference Availability

James, L. A. and Blackburn, L. D., "Technical Progress Report on BWIP Canister Materials Crack Growth Study for FY 1983," SD-BWI-TI-165, January 1984.

DATE REVIEWED: 10/6/87; Revised 12/27/87

TYPE OF DATA

(1) Scope of the Report

Experimental laboratory data

(2) Failure Mode or Phenomenon Studied

Fatigue crack growth

MATERIALS/COMPONENTS

ASTM A36 steel
ASTM A27 Grade U-60-30 steel
ASTM A387 Grade 9 steel
The materials are proposed as candidates for waste container vessels.

TEST CONDITIONS

(1) State of Materials Tested

ASTM A36 is a wrought steel.
ASTM A27 is a cast steel.
ASTM A387 is a wrought steel. It was austenitized at 1650°F for 60 minutes and furnace cooled; transformed at 1300°F for 250 minutes and air-cooled. No subsequent tempering was performed.

Two tables contain the A36 and A387-9 compositions and mechanical properties. For A36 (Pohang heat Y45659): composition (weight %) C = 0.15, Si = 0.2, Mn = 0.96, P = 0.23, S = 0.014, Cu = 0.02; yield strength = 45.8 ksi, ultimate strength = 67.8 ksi, elongation = 28.0 %, reduction in area not given. For A387-9 (Armco heat 45862): composition (weight %)

C = 0.11, Si = 0.23, Mn = 0.59, P = 0.012, S = 0.013, Mo = 0.94, Cr = 8.70; yield strength 75.8 ksi, ultimate strength = 99.5, elongation = 22.0 %, reduction in area = 65.7 %.

(2) Specimen Preparation

Compact Specimens, type C(T) were prepared for E647-83 fatigue tests in air, after precracking of the specimens (A27, A36, A387). (Specimen dimensions are given.) Initial K-levels were 30, 40, and 60 MPa x $m^{1/2}$.

(3) Environment of the Materials being Tested

Air at test temperatures of either 150 or 250°C.

METHODS OF DATA COLLECTION/ANALYSIS

The specimens were subjected to fatigue-crack propagation (FCP) tests in accordance with ASTM E647-83 in servo-hydraulic testing machines operating in load control. Sinusoidal waveforms at a cyclic frequency of 600 cpm were employed, and the stress ratio ($R = K_{min}/K_{max}$) was 0.05 for all tests. Specimens were enclosed in air-circulating furnaces. Crack lengths were determined periodically throughout each test by means of a travelling microscope. Crack growth rates (da/dN) were calculated using the "secant method" and the stress-intensity factor range (∓K) using the relationship given in ASTM E647-83.

AMOUNT OF DATA

Five figures are given in which are plotted the logarithm of the fatigue-crack-propagation (FCP) rate (da/dN) as a function of the logarithm of the stress-intensity factor range (∓K). The units of da/dN are inches/cycle and of ∓K are psi.$in^{1/2}$.
Figure 1 is titled "Fatigue-Crack Growth Behavior of Wrought A36 Steel Tested in an Air Environment at 150°C." Figure 2 is titled "Fatigue-Crack Growth Behavior of Wrought A36 Steel Tested in an Air Environment at 250°C." Figure 3 is titled "Fatigue-Crack Growth Behavior of Wrought A387 Grade 9 Steel Tested in an Air Environment at 150°C." Figure 4 is titled "Fatigue-Crack Growth Behavior of Wrought A387 Grade 9 Steel Tested in an Air Environment at 250°C." Figure 5 is titled "Fatigue-Crack Growth Behavior of Cast A27 Grade U-60-30 Steel Tested in an Air Environment at 150°C." Individual regression lines for the various material/temperature combinations are plotted in Figure 6 titled "Comparison of the Fatigue-Crack Growth Behavior of Steels Tested in an Air
Environment." A table, Table 5 -- Crack Growth Equation Constants, gives the constants in the crack growth equation for these experiments.

UNCERTAINTIES IN DATA

Cyclic loads were controlled to within better than 1%. Furnace temperatures were controlled within ±1.5°C.

DEFICIENCIES/LIMITATIONS IN DATABASE

The minor differences in FCP behavior between the various material/temperature combinations at lower values of ΔK should not be interpreted as suggesting the superiority of one alloy over another. Testing in aqueous environments is necessary.

KEY WORDS

Experimental data, linear-elastic fracture mechanis (LEFM), fatigue crack propagation ASTM E647-83, laboratory, high temperature, ambient temperature, stainless steel, carbon steel, A36, A27 Grade U-60-30, A387 Grade 9, annealed (austenitized and transformed), cast (A27), wrought (A36), standard compact, precracked, crack extension, fatigue (high cycle), cracking.

GENERAL COMMENTS OF REVIEWER

This is a non-critical review.

RELATED HLW REPORTS

SD-BWI-TI-120
SD-BWI-TS-012
RHO-BW-SA-560P

APPLICABILITY OF DATA TO LICENSING

Ranking: key data ( ), supporting data (X)

(a) Relationship to Waste Package Performance Issues Already Identified

This document is related to BWIP ISTP issue, 2.2.3, identification of the possible mechanical failure modes for the waste package container. The failure mode being tested here is fatigue crack growth at elevated temperatures in air.

(b) New Licensing Issues

(c) General Comments on Licensing

NBS Review of Technical Reports on the High Level Waste Package
for Nuclear Waste Storage

DATA SOURCE

(a) Organization Producing Report

Rockwell International, Rockwell Hanford Operations, Richland, Washington.

(b) Author(s), Reference, Reference Availability

Duncan, D. R., James, L. A., and Pitman, S. G., "Status of Environmentally Assisted Cracking Studies by the Basalt Waste Isolation Project," RHO-BW-SA-560P, March 1986.

DATE REVIEWED: 10/6/87; Revised 12/30/87

TYPE OF DATA

(1) Scope of the Report

Experimental determination of slow strain rate and fracture mechanics data.

(2) Failure Mode or Phenomenon Studied

Environmentally-assisted cracking (EAC), defined as cracking by simultaneous action of an aggressive media and a tensile stress. In this report, EAC is used to mean both stress corrosion cracking and hydrogen embrittlement.

MATERIALS/COMPONENTS

1020 carbon steel
A27 grade 60-30 carbon steel
A387 grade 9 low-alloy steel (9 Cr-1 Mo)
Oxygen-free high-conductivity (OFHC) copper (UNS C10200)
Cupronickel 90-10 (UNS C70600)

The above are candidate container materials.

TEST CONDITIONS

(1) State of the Material being Tested

1020 carbon steel was wrought (hot-rolled).
A27 carbon steel was as-cast.
A387 steel was tempered (720°C-61 min) plate.
OFHC copper was wrought "half hard".
90-10 cupronickel was annealed to a "soft" temper.

(2) Specimen Preparation

For slow strain rate tests no information is given.

For fracture mechanics testing, specimens were modified-wedge/open-load (MWOL) design which were precracked in fatigue about 1.3 to 1.5 cm beyond the mechanical notch to produce a sharp, natural crack. The compliance (load to produce a given displacement) of each cracked specimen was experimentally determined to calibrate each specimen prior to application of test loads. Displacements were measured with a clip gage constructed to the requirements of ASTM E399. Specimen compliance calibration was used to achieve the desired initial stress-intensity (K) level prior to testing.

(3) Environment of the Material being Tested

Groundwater simulating that of the basalt strata, i.e., Grande Ronde groundwater from the Cohassett flow was mixed with crushed basalt.

METHODS OF DATA COLLECTION/ANALYSIS

Procedure for slow strain rate tests:
The tests were performed in a refreshed autoclave system with a gear-driven mechanical loading device. Groundwater solution was pumped to the autoclave at 9 to 35 ml/h, from a reservoir where it was sparged with argon or with a mixture of argon and 20% oxygen. The inlet water flowed through crushed basalt before contacting specimens. Slow strain rate tests were also conducted in air. Test temperatures were 100, 150, and 200°C. Specimens were strained to failure at rates of 1×10^{-4}/s, 1×10^{-6}/s, and 2×10^{-7}/s. Yield and ultimate strengths were calculated from the load and displacement measurements. The elastic limit was taken as the yield strength rather than a 0.2% offset value due to limited resolution of the displacement measurements. Fractured specimens were cleaned in an inhibited acid solution and examined macroscopically for cracking or pitting. Selected specimens were examined by scanning electron microscopy.

Procedure for fracture mechanics tests:
During static-load testing, specimens were loaded to the desired K value by torquing the loading bolt until the desired value of crack mouth opening displacement was reached. Strips of plastic tape were employed on both specimen faces, and the notch and crack area were filled with groundwater during loading. Loaded test specimens (with tape removed) were placed in an autoclave partially filled with groundwater. The autoclave was then filled with groundwater, crushed basalt, and bentonite and brought to 100 atmospheres (10.1 MPa) pressure and the one of the test temperatures (150 or 250°C). Autoclave contents were essentially static during testing. After exposure, posttest compliance measurements were made. Specimens were immersed in liquid nitrogen to embrittle them, and then fractured along the line of the existing crack. Crack length was measured optically and crack surfaces were examined.

Cyclic loading specimens were tested according to ASTM E647 in servo-hydraulic machines operated in load-control mode. Sinusoidal wave forms with stress ratios of 0.05 were used. Cyclic frequencies ranged from 0.1 to 10 Hz. Tests were performed in air, vacuum, and simulated basalt groundwater, at temperatures of 150 and 250°C. Tests in groundwater were conducted at 68 atmospheres (6.9 MPa) in low-flow autoclaves.

AMOUNT OF DATA

There are seven tables.
Table I--"Composition of Actual and Synthetic Grande Ronde 4 Groundwater Solution," lists 8 constituents in mg/l and pH.
Table II--"Composition of Materials in Slow Strain Rate Tests," lists element composition (weight %) for the five tested alloys.
Table III--"Composition of Synthetic Grande Ronde 2 (GR-2) Groundwater Solution," lists 11 constituents in mg/l and the pH.
Table IV--"Composition of Materials in Fracture Mechanics Tests," lists composition in weight % for two steels.
Table V--"Equilibrium Groundwater Composition," lists 8 constituents in mg/l and the pH for the water used in the static loading tests.
Table VI--"Results of Slow Strain-Rate Tests on BWIP Candidate Containers." Data for five alloys are listed: temperature (°C), strain rate (s), elongation (%), reduction of area (%).
Table VII--"Static Load Test Conditions," lists conditions for two steels in three tests. Data given are precrack maximum K and initial test K (both in $MPa \bullet m^{1/2}$).

There are ten figures.
The first two are schematic diagrams of fracture mechanics data.
Figure 1--"Schematic Relationship Between Applied Stress, Crack Size, and Threshold Stress Intensity Factor."
Figure 2--"Threshold Stress Intensity Factor and Fracture Mechanics Data."

The next five figures are graphs containing slow strain rate data. Reduction in area in % (0 to 70) is plotted against strain rate in s^{-1} (10^{-7} to 10^{-3}).
Figure 3--"Slow Strain Rate Results for 1020 Wrought Carbon Steel (150°C)."
Figure 4--"Slow Strain Rate results for A27 Case Carbon Steel (150°C)."
Figure 5--"Slow Strain Rate Results for A387 Low-Alloy Steel (150°C)."
Figure 6--"Slow Strain Rate Results for 90-10 Cupronickel (100 and 200°C)."
Figure 7--"Slow Strain Rate Results for Oxygen-Free High-Conductivity Copper (100 and 200°C)." In this graph the reduction in area ranges from 0 to 30.

The last three figures contain fatigue crack growth data obtained in the cyclic tests. Fatigue crack growth rate, da/dN, in mm/cycle (10^{-6} to 10^{-3}) is plotted versus stress intensity factor range, ∓K, in $MPa \bullet m^{1/2}$.
Figure 8--"Fatigue Crack Propagation in Carbon Steels at 250°C," shows data for A36 in air, vacuum and a groundwater, and for A27 in the groundwater.
Figure 9--"Fatigue Crack Propagation in A36 Steel at 150°C," shows data in air, vacuum, and groundwater.
Figure 10--"Fatigue Crack Propagation in A387 Steel at 250°C," shows data in air and vacuum.

UNCERTAINTIES IN DATA

For cyclic-load fracture tests, the loads were controlled to within 1% or less.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Experimental data, linear-elastic fracture mechanics (LEFM), microscopy, visual examination, slow strain rate, laboratory, air, basalt composition, simulated groundwater, Cl, SO_4, H_3SiO_4, Na, basalt, bentonite, high temperature, high pressure, hydrostatic head, basic (alkaline) solution (pH >7), static (no flow), dynamic (flow rate given), copper base, carbon steel, low-alloy steel, 1020 carbon steel, A27, A387, OFHC Copper (UNS C10200), Cupronickel 90-10 (UNS C70600), annealed (Cupronickel), cast (A27), wrought (1020) (OFHC Copper), tempered (A387), slow strain rate, bolt or wedge loading, prestressed (during exposure), crack elongation, corrosion (stress cracking) SCC, fatigue (corrosion), cracking (stress corrosion) SCC, cracking (environmentally assisted)

GENERAL COMMENTS

This is a non-critical review. A more complete discussion of the work reported here is to be found in the related HLW reports listed.

RELATED HLW REPORTS

SD-BWI-TI-152
SD-BWI-TS-008
SD-BWI-TI-120
SD-BWI-TS-012
SD-BWI-TI-165

APPLICABILITY OF DATA TO LICENSING
Ranking: key data ( ), supporting data (X)

(a) Relationship to Waste Package Performance Issues Already Identified

This document relates to BWIP ISTP issue, 2.2.4, what are the potential corrosion failure modes of the waste container. Specifically, the possibility of environmentally-assisted cracking (EAC) was investigated in this report for a series of possible container materials.

(b) New Licensing Issues

(c) General Comments on Licensing

MRS Symposium 1987
Symposium P: Scientific Basis for Nuclear Waste Management

NBS staff members who attended the annual Materials Research Society Symposium in Boston, MA, were Mr. Ed Escalante, Dr. Helen Ondik, Dr. Ernie Plante, Dr. Rick Ricker, and Ms. Jill Ruspi. Symposium P, "Scientific Basis for Nuclear Waste Management," was held from November 1 - December 3, 1987. Short presentations of the content of the papers and posters are given below. Approximately 90 papers will be published in the MRS Symposia Proceedings, Volume 84, Scientific Basis for Nuclear Waste Management XI, and technical evaluation can be made after publication.

The paper P.9.1., by J. K. Bates, "Methods to Evaluate the Long-Term Performance of Waste Package Interactions," addressed many of the issues most frequently discussed at this symposium. The issues raised in Bates' paper were alluded to by a number of authors and also during the question periods following papers. Bates discussed methods which should be used in evaluating long-term performance. He emphasized the necessity of having a combination of experiment with modeling and of modeling with verification. For experiments, he advocates a "what if" approach which would take into account all possible conditions and all possible effects. Bates believes that the third part of the long-term performance studies, verification of the model, is currently the weakest area of performance evaluation.

Session P1--Low-Level Waste Studies

P.9.6. Baker, R. S., "Experimental Glass-Ceramic Products to Immobilize ICPP HLW."

The last paper of the low-level waste session dealt with high-level waste from the Idaho Chemical Processing Plant (ICPP). The project aim is the immobilization of the waste in glass-ceramic form to provide maximum waste density and minimum volume. Roseanne S. Baker of Westinghouse Idaho Nuclear Co., Inc. discussed the formation of multiphase glass-ceramic products by hot-isostatic pressing (HIP) at 20,000 psi of the calcined fuel waste with glass frits, silica or yttria. Additives can invade the cracks caused by calcining. The procedure provides for high (60-80%) waste content. Although HIP is an established technology, the following questions must still be answered for application to HLW: what are the redox requirements, what are the best temperature and pressure ranges, and what is the effect of particle size on processing and product properties. The process must be developed further (for a range of waste compositions and to maximize product durability, and also to be able to change the amount of the frit without changing the composition).

Session P2--Plenary Session: Scientific Basis for Nuclear Waste Management

P.2.1., Grenthe, I., "Evaluation of the Chemical Environment Within Nuclear Waste Packages."

Papers in the plenary session dealt with the planned approach of assessing long-term performance of the repository. Ingmar Grenthe of the Royal Institute of Technology, Stockholm, discussed the factors to be considered in modeling for a repository situated in crystalline rock, with bentonite backfill and copper or mild-steel waste containers. The factors include thermodynamic modeling of groundwater/bentonite interactions, the differing mechanisms and products of copper versus those of mild-steel, and the effect of radiolysis in the canister when penetrated by water. A suggested canister design might have copper as a durable outer casing with iron or ferrous oxide as a reducing pillar inside. The iron or ferrous oxide next to the fuel would be an efficient oxygen scavenger to prevent corrosion of the copper.

P.2.2., Marsh, G. P., "Prediction of Long Term Metal Corrosion of Nuclear Waste Disposal."

George P. Marsh of the Harwell Laboratory in Oxfordshire indicated the need for a combination of experiments and modeling in order to provide convincing answers to questions of long-term behavior and predictions of performance. The often made assumption that the environment will not change over time is not valid. The fundamental problem is in deciding how to extrapolate from short-term experiments to long-term service conditions. Marsh's answer is to do extrapolation on a mechanistic basis. Once the mechanism of the reactions taking place is understood, then a mathematical model of the process can be formulated. This model must be supplemented by more experimentation. Selection of the data for use with the model is critical. The model can provide a corrosion allowance and further experiments may indicate that a new model is needed. The modeling results may show too much uncertainty, Thus, the process is cyclic. Examples have shown that in the case of localized corrosion data, these data are valid for only 1/10 of the passive corrosion period. Extrapolated data based on these values tend to give overly pessimistic predictions.

P.2.3., Johnson, L. H., "Characterization and Evaluation of Spent Fuel Performance Under Disposal Conditions."

Lawrence H. Johnson of the Whiteshell Nuclear Research Establishment, Manitoba, reviewed a number of studies evaluating spent-fuel performance performed in different countries. For Zircaloy-clad fuel, corrosion can be rapid in mildly saline groundwater and it proceeds from the inside out, once the initial failure has occurred. The knowledge is only qualitative. Attack is known to occur first at fuel/grain boundaries, but what is at the grain boundaries is unknown. Fission gas bubbles form at boundaries and provide sites and pathways for preferential attack. The fuel is subject to leaching at the grain boundaries followed by dissolution of the matrix. The preparation of samples for experimental studies is too highly oxidizing causing invalid reducing experiments. Results for unoxidized UO_2 fuel are too low. To illustrate how highly dependent performance is on the specific environment, Johnson mentioned that radionuclides are released in both saline and distilled water. Radionuclides leached more in saline solution than in distilled water; the saline etches and attacks the grain boundaries and grain dissolution results. For mass transport modeling, the liquid flow rate directly affects the dissolution rate of UO_2. The UO_2 reactivity varies with the form, whether spent fuel, sintered disk, or single crystal. Other factors which make modeling difficult include (1) the fact that reducing conditions significantly decrease dissolution rates of used fuel, (2) incomplete data for the grain boundaries of the spent fuel and the release kinetics, and (3) the need to take into account the effect of radiolysis in reducing environments.

P.2.4., Stephens, K. W., "Technical Challenges Facing Regulators -- Assessment of Long-Term Materials Performance."

Kenneth Stephens of Stephens and Associates discussed the technical issues as seen from the regulators' perspective. He named (1) the problems of using long-term extrapolation of short-term data, (2) the degree to which models must represent reality, and (3) the question of how to validate predictive computer codes as important issues facing regulators. The following principles must be kept in mind: (1) non-technical issues affect technical decisions and these issues must be considered by researchers, (2) decisions are made by people based on their perceptions of reality and not necessarily on reality itself, and (3) people must discuss their differing perceptions with each other to resolve conflicts when decisions are made.

P.2.5., Pigford, T. H., "Radionuclide Transport in Geologic Repositories: A Review."

Thomas H. Pigford of the University of California, Berkeley, reviewed radionuclide transport in repositories. One of his major points was that he does not see the program obtaining good data on container failure, especially with regard to short-term release of radionuclides. He discussed the following items which must be considered in applying mass transport theory and about which faulty assumptions are often made:

1. the effect of the liquid-filled annulus between the waste fuel and the rock of the repository,
2. the effect of flow direction and geometry,
3. hydrodynamic diffusion,
4. the effect of radioactive decay,
5. local sorption equilibrium,
6. linear sorption, constant distribution coefficient, constant retardation coefficient,
7. surface diffusion,
8. interference from other waste packages,
9. porosity of fractured rock,
10. constancy of temperature,
11. constancy and uniformity of chemical environment,
12. the absence of any radioactive decay precursors.

The Plenary Session included a panel discussion at the end. Questions were raised concerning the validity of much modeling and the value of modeling versus spending the money on heavy containment for the long term. The question was also raised about the problem of predicting an unlikely perturbation of conditions or event in the repository even though thermodynamics predicts long-term viability for a design. Pigford suggested that well-controlled laboratory experiments and a valid theory to predict the future are both necessary in producing valid models for long-term predictions.

Session P3--Migration and Transport Studies

P.3.1., Vandergraaf, T. T., "Laboratory Radionuclide Migration Experiments at a Scale of 1 Metre."

A paper given by Tjalle T. Vandergraaf of Whiteshell Nuclear Research Establishment, and co-authored by staff of Whiteshell and Battelle Memorial Institute, discussed results of six radionuclide migration experiments using large quarried granite blocks; two halves providing a channel for the flow. Although the width of the channels varied, these experiments found that 10 percent of the channels carry most of the flow. This results in high velocity for small surface volumes. The laboratory migration studies must consider both static and dynamic sorption, radionuclide colloid formation, diffusion, and fracture surface analysis. The results indicated that the elution profile (volume versus time) reaches a steady-state volume flow. The most important factors to look for in channel studies are (1) water flow rate, (2) wetted surface in a channel, (3) diffusivity in the rock matrix, and (4) sorption coefficient of the rock. There is no real effect of diffusion seen since there is no change in the elution profile with the flow rate. In the future, two-dimensional scanning of the fracture surface is planned.

P.3.2., Moreno, L., "Channeling and Its Consequences for Radionuclides Transport."

Moreno's modeling study shows that, unlike conventional beliefs, most radionuclide transport is through a limited number of fractures in the rock, and gives support to field experiments showing higher flow rates where fewer channels exist in the stone (see P.3.3). In addition to uneven flow through channels, Moreno concludes that (1) most radionuclides are carried by channels 1m wide or less, (2) some tunneling does occur, (3) most of the radionuclide flow is carried by only a few channels, (4) radionuclide decay is less in fast channels, and (5) the concentration of radionuclides through the channels is determined by sorption capacity of the stone, the amount of wetted stone surface, and water-flow rate.

P.3.3., McKinley, I., "The Radionuclide Migration Experiment at Grimsel, Switzerland."

Ian McKinley and co-workers at EIR, Switzerland, are performing in-situ radionuclide migration experiments in an underground laboratory in the Alps. Their results indicate that about 10 percent of the channels in the rock take most of the flow rate. The data indicate that, for transport modeling, the most important entities to assess are those cited in the discussion above. Including dispersion in the calculations does not make a large difference in the results.

P.3.4., Birgersson, L., "Diffusion in the Matrix of Granitic Rock Field Test in the Stripa Mine."

This study shows that disturbance of the diffusion characteristics of the rock by drilling experiments, a major concern, is limited to within two-hole diameters of the drilling. Outside of this range, the laboratory diffusion data agree with the field diffusion experiments, which show that radioactive tracers migrate through undisturbed rock with diffusivities of 10^{-2} to $10^{-9} m^2/s$. The extent of movement of these tracers is related to the sorption properties of the rock resulting in migration distances of 60 to 400 mm in 3.5 years in granite.

P.3.5., Abelin, H., "3-Dimensional Migration Experiment, Large Scale In Situ Test."

These field results were obtained from drifts 360 m below ground. The walls of these drifts were covered with 375 plastic sheets which collected liquids from the sections of the drift wall. After characterizing the flow of water for 6 months, radioactive tracers were injected into the stone at various locations. The water collected from the sheets was then monitored for tracers. The results show that: (1) water flow is uneven; 12 sheets collected 50 percent of the water, (2) there is no correlation between fracture length and flow rate, (3) channeling persists over distances up to 60 m, (4) models in the literature do not take into account all processes that affect transport, and this omission results in poor correlation to field data.

P.3.6., Nowak, E. J., "Brine Transport Studies in the Bedded Salt of the Waste Isolation Pilot Plant (WIPP)."

E. J. Nowak of Sandia National Laboratories discussed brine transport of the Waste Isolation Pilot Plant (WIPP). Current tests are designed to extend earlier small-scale tests and to emulate repository conditions by placing heaters in the bore holes in the bedded salt of the WIPP. The experiments show that the Darcy flow of interstitial brine dominates brine transport in the bedded salt. The data for cumulative water measured versus time for heated (isothermal) flow is a straight line whereas for the unheated case, the line flattens and the slope decreases. The data for the flow rate versus time show a large amount of scatter for both the heated and unheated cases. For the heated bedded salt, the flow rate peaks at about 100 days and remains fairly constant after that. For the unheated case, the thermal effect is over after 100 days and the flow rate decreases. The results to be modeled, therefore, are the 5-15 grams/day (average 10 grams/day) flow rate and the approximately 10 grams/day flow rate after heating for Darcy flow in an elastic porous media. The fit of the model used with the data is a fair fit for long-term inflow and is within reasonable values for permeability, but for the heated model the match with viscosity alone is not good. Thermal expansion must be included. The heat source increases the inflow. For the future, the isothermal model must be developed further, and pore pressure must be measured to understand the effect of excavation on the bed properties.

Session P4--System Modeling

P.4.1., Aidun, C.K., "Radionuclide Transport Through Perforations in Nuclear Waste Containers."

In a paper about radionuclide transport through container perforations, Cyrus Aidun of Battelle Project Management Division stated that the assumptions used in earlier modeling work included that of zero wall thickness. This model provides values that are too large, and the model increases in overprediction as the radius of the hole approaches zero. The model predicts a greater release of radionuclides from a large number of small holes than would be released from uncontained bare fuel. A better set of results is obtained by investigating the effect of wall thickness using a flat-plate approximation, which can be used since the dimensions of any hole produced by localized corrosion are expected to be very much less than the dimensions of the container. The resistance analog model derived from the solution of the steady-state diffusion equation for the concentration field provides for a release rate as a function of wall thickness as well as hole radius and the radionuclide concentration inside the container. Since, in reality, the holes will not be uniform in size, a statistical approach is needed in the modeling. Although the zero-wall-thickness model is not good for small holes, the finite-wall-thickness model is not good for varied hole radius, therefore, further work is needed.

P.4.2., Ross, B., "Gas-Phase Transport of Carbon-14 Released from Nuclear Waste Into the Unsaturated Zone."

Benjamin Ross of Disposal Safety Inc. spoke about modeling gas-phase transport of ^{14}C in unsaturated rocks such as the tuff at Yucca Mountain. The equations needed to express the transport must include parameters describing the movement and transfer of ^{14}C, the chemical environment, and the air flow velocity for advection. The quantities to be measured for inclusion in the model equations are tortuosity, air-filled porosity, diffusivity, and the volume of the moisture content. The gas velocity depends on the difference between the dissolved concentration and the solid-phase concentration. The gas flow will be driven by the repository heating, and the topographic effects of cold low-humidity air in winter and warm high-humidity air in summer. These factors must be combined with the chemical equilibria but there is a question of which equilibrium situation to consider: (1) the dissolution of calcite dissolved by carbonic acid, (2) the calcium and alkali produced by tuff weathering, or (3) the undersaturation of water by calcite. A good model should predict results which can be verified by measurement. The values to measure to check the model are (1) total CO_2, (2) natural ^{14}C, (3) water chemistry, (4) ^{13}C content, (5) ^{14}C in calcite, and (6) observed mineral assemblages. The questions still open for application of the model include the equilibrium chemistry, the advective transport, and the importance of the repository heat, its rate of transfer, and the effect on container life.

P.4.4., Carnahan, C. L., "Simulation of Effects of Redox and Precipitation on Diffusion of Uranium Solution Species in Backfill."

Migration of uranium in solution through packing or backfill is affected by the extent of precipitation the uranium undergoes as it moves through the material. The reducing or oxidizing conditions of the environment play an important role in this precipitation process. The results of these simulated experimental conditions show that (1) there was no expanding front in the presence or absence of precipitation, (2) in the absence of conditions for precipitation of uranium, Eh and pH had no effect on the total uranium concentration in solution, and (3) with conditions for precipitation, the uranium collected near the source.

P.4.6., Garisto, N. C., "A Vault Model for the Assessment of Used Nuclear Fuel Disposal in Canada."

Assuming titanium-based alloys for the containers, Garisto's model considers early container failures that will occur due to manufacturing defects, followed by a period with minimum failures as corrosion processes progress. Eventually, release rates increase as container failure occurs due to corrosion. Initial radionuclide release rates are high as soluble materials diffuse away from the container. This period is followed by a long period of slow release from less soluble species.

Session P5--Poster Session

In general, the poster session was not as valuable as the regular sessions. Unlike the 1986 MRS meeting, this year all symposia with poster sessions were held simultaneously in the same area. Overcrowding, overheating, noise, and the fact that a number of the proposed posters for Symposium P were not presented, all contributed to an unsatisfactory experience. Twenty-nine poster papers had been scheduled but at least nine were omitted.

P.5.1., Bates, J. K. and Gerding, T. J., "The Performance of Actinide-Containing SRL 165 Type Glass in Unsaturated Conditions."

A test was performed in unsaturated conditions which produced data that is expected to be used in the licensing process. A parametric test was performed to study the effect of varying physical parameters. These parameters were fixed in an unsaturated test. The parameters may affect the reaction process. An analog test acts as a link between the unsaturated test and the repository environment to demonstrate the relevance of the unsaturated test to repository conditions.

P.5.3., Caurel, Jean, "Mineral Phases Identification Along Two Profiles from the LWR Reference Glass. Use of an X-ray Linear Local Detector."

Jean Caurel of the University of Poitiers showed the results of x-ray identification of the mineral phases in glass for LWR waste use which was leached in distilled water. A specimen leached at 300°C exhibits a thick alteration profile with the mineral sequence varying from fibrous zeolites to allite. The mineral phases show a gradual dehydration outward with a gain of sodium and a loss of calcium. All phases identified are metastable. A thick alteration profile is characteristic of the corrosion process.

P.5.5., Feng, X., "Systematic Composition Studies on the Durability of Waste Glass WV205."

Xiangdong Feng of Catholic University showed work on the durability of West Valley glass 205. His conclusions were (1) a high-oxidation condition during melting produces a more durable glass, (2) the addition of oxides of zinc, titanium, copper, or nickel enhances corrosion rates, (3) the addition of alumina increases the durability, and (4) models such as those used by Jantzen and Plodinec are useful in understanding these effects.

P.5.13., Blasi, P., Ceccone, G., and Mammarella, L., "Borosilicate HLW Glass Leaching in Silica Saturated Solution."

Borosilicate HLW glass leached in a silica saturated solution showed a constant concentration of Na^+H suggesting that H^+ rather than H_3O^+ is the migrating species. Dissolved SiO_2 effects initial stage of dissolution, but has no effect on Na and B release. SiO_2-Al_2O_3 formed after 7 days does not appear to influence sodium or boron release nor Na and H^+ interdiffusion. The surface layer does not appear to be an effective diffusion barrier, although the rate of weight loss slows down because of the precipitated surface layer.

P.5.18., Mouche, E., "Aqueous Corrosion of the French LWR Solution Reference Glass: First Generation Model."

Emmanuel Mouche of the Commission of Atomic Energy, France, provided the following assumptions to be made in modeling with regard to the gel-glass interface formed in aqueous corrosion of the French glass for LWR waste: (1) the thermodynamic equilibrium between silicon in solution indicates that the gel plays an important part in dissolution kinetics, (2) the high silicon concentration in the gel seems to be due mainly to chemisorption of diffusing silicon on the gel, which implies that a chemisorption term in the silicon diffusion coefficient will have to be included in a more advanced model, (3) this equilibrium indicates that a system evolves towards a dissolution steady-state governed by the gel rather than a thermodynamic equilibrium imposed by the glass, (4) the most difficult theoretical problem consists in proving by an expression of the gel free energy that the silicon chemical potential is lower in the gel than in the glass.

P.5.20., Pescatore, C. and Sastre, C., "Mass Transfer from Penetrations in Waste Containers."

Pescatore and Sastre evaluated the conclusion of previous studies that a larger release rate will occur from small penetrations in a waste container than from bare waste form. The earlier studies calculated the release rate from a single penetration in the container and then simply multiplied this rate by the number of penetrations. As a result, the predicted release rate for a large number of holes in a container exceeds the predicted release rate of bare fuel. However, Pescatore and Sastre point out that this process assumes that the release rate from a penetration is not influenced by the presence of other penetrations nearby. This assumption is not valid as the concentration gradients existing in the media will interact as the number of the penetrations increases and their spacing decreases. As pointed out by Pescatore and Sastre, the release rate from the penetrations in greater than the rate from a bare planar surface because of the spherical geometry of the concentration gradients versus the planar geometry of the bare surface. However, when concentration gradient interactions are taken into account, calculations indicate that as the number of penetrations increases the concentration gradients merge and a transition from spherical to planar geometry occurs. As a result, the rate of release from a container with penetrations in it will increase as the number of penetrations in it increases until the concentration gradient around the penetration overlap, and then the release rate will asymptotically approach that of bare fuel.

The conclusions reached by Pescatore and Sastre appear to contradict the information presented by C. K. Aidun in P.4.1.

P.5.21., Strachan, D. M., "A Comparison of the Performance of Nuclear Waste Glass by Modeling."

A paper by Denis M. Strachan, Pacific Northwest Laboratory, in collaboration with Bernd Grambow, Hahn-Meitner-Institute, Berlin, compared the performance of nuclear waste glasses by means of modeling. The following was learned in applying the geochemical code PHREEQE and the glass dissolution model GLASSOL to the glasses JSS-A, SRL-131, and PNL 76-68: (1) in short-term tests or under highly diluted conditions the initial solution composition is quite important, but the long-term performance seems to be only slightly affected by the initial solution composition, (2) the most critical parameter for extrapolating laboratory results to repository performance is the long-term rate, (3) the models can be used to calculate behavior of glass in contact with aqueous solution over long time periods, (4) a generalized set of precipitation phases is needed, (5) JSS-A and SRL-131 have similar durability in short-term tests, but modeling for long-term performance shows the JSS-A to be an order of magnitude more durable that SRL-131, and (6) silicic acid appears to be the key species in dissolution mechanisms of silicate glasses. Several key studies remain to be performed on nuclear waste glasses before modeling can be extended to relevant time periods.

P.5.22., Torstenfelt, Borje, "Size and Density of a ^{242}Pu Colloid."

A cooperative effort, between Los Alamos National Laboratory and Chalmers University of Technology, Goteborg, Sweden, was reported by Borje Torstenfelt on the study of the size and density of a ^{242}Pu colloid. The poster gave the following summary: (1) a ^{242}Pu colloid was observed using autocorrelation photon spectrometry, (2) a mean diameter of 2.9 nm was deconvoluted from the autocorrelation spectrum; this was the smallest colloid observed to date with the Los Alamos autocorrelation photon spectrometer, (3) the colloid was found to settle 1.8 cm under ultracentrifugation at 40,000 rpm for 2 hours, (4) a density of 9.0 g/cm^3 ± 2 g/cm^3 was obtained from the sedimentation formula. This is nearly 20% lower than the estimated density of crystalline PuO_2, 11 g/cm^3, (5) the diameter of the ^{242}Pu colloid is nearly two orders of magnitude smaller than that of the ^{239}PU colloid prepared by the same technique; recent experiments have obtained a similar density for ^{239}Pu colloids.

P.5.24., Zavoshy, S. J., "High-Level Waste Dissolution and Secondary Mineral(s) Formation and Dissolution."

In a poster paper discussing high-level waste dissolution and secondary mineral formation and dissolution, S. J. Zavoshy of Bechtel National formulated a mathematical model of dissolution that includes mineral formation. The test was performed to investigate the influence of secondary precipitate formation on the waste dissolution rate. The formation of a second precipitate leads to a constant dissolution rate. The following conclusions were posted: (1) In a static experiment, a temperature super-saturation can be achieved. (2) Dissolution of highly soluble species is congruent with the main component of the matrix. (3) For a low-solubility species, the surface-liquid concentration is almost equal to the species solubility limit in groundwater. (4) The mass flux is independent of the species retardation coefficient and is determined by the matrix dissolution rate.

P.5.25., Zhou, Z. and Fyfe, W. S., "Comparative Experimental Study of Glass Stability in Sea Water and Distilled Water."

This test studied the corrosion of PNL 76-68 and ABS 118 glasses. Corrosion rates are less in seawater than in distilled water. The conclusions suggest that the reaction $SiONa + H^+ \rightarrow SiOH + Na^+$ is depressed in seawater.

Session P6--Near-Field Chemistry

P.6.1., Wickberg, P., "The Natural Chemical Background Conditions in Crystalline Rocks: Results from the Swedish Site Investigations."

Using in-situ measurement techniques, Wickberg has succeeded in measuring ferric concentrations to a depth of 1000 m. His results indicate that ferric concentrations are high near the surface and rapidly decrease with depth as a result of decreasing Eh with depth. Eh is controlled by soluble minerals in the rock.

P.6.2., Grandstaff, D. E., "Results of Basalt-Water Experiments: Implications for Nuclear Waste Disposal."

Autoclave experiments show that basalt maintains a chemically stable environment. A basalt-water environment at high termperature (100 - 300°C) and high pressure (50 MPa), after reaching equilibrium, was chemically upset by injecting air saturated solution. However, within hours the conditions returned to pre-equilibrium conditions.

P.6.4., Reed, D. T., "Effect of Gamma Radiation on Moist Air Systems."

Donald T. Reed of Argonne National Laboratory in collaboration with Lawrence Livermore National Laboratory conducted a literature survey on the effect of gamma radiation on moist air systems. The results of a study to find the effects of the formation of NO_x, for instance, in moist conditions indicate that nitric acid formation is solely a gas-phase problem and will not occur in the aqueous solution present in the repository. Also, in the air-saturated environment no ammonia will form. Ammonia formation would be a problem, for example, as it causes cracking in copper.

P.6.7., Jacobsen, J. S. and Carnahan, C. L., "Numerical Simulation of Alteration of Sodium Bentonite by Diffusion of Ionic Groundwater Components."

Jacobson and Carnahan used the TIP computer program (a transport code modified to include ion exchange and aqueous complexation reactions) to consider alteration of Na bentonite by ion exchange with groundwater species (Na_+, Mg_{+2}, K_+) to form mixed Ca-Mg-K-Na bentonite. They concluded that alteration takes place slowly, and they suggest adding effects of precipitation, dissolution, and redox conditions to their model. The basis of their work is that the rate of radionuclide migration will differ for Na bentonite and the altered Na bentonite.

P.6.8., Sharland, S. M., "Chemical Perturbations in the Disturbed Zone of a Nuclear Waste Repository."

S. M. Sharland of Harwell spoke about the chemical perturbations in the disturbed zone (caused by the engineered barriers) of a repository in which the surrounding rock is clay. CHEQMATE (Chemical Equilibrium with Migration And Transport Equations) is a modeling code which couples ionic migration and chemical equilibrium to examine the spatial and temporal evolution of various aspects of the chemical environment. One of the environmental changes examined by the model is that of the pH in the host geology. The pH at the clay is essentially neutral, but in the repository area the pH is high. The pH change can affect the physical properties of the clay, such as porosity and permeability, and the chemical properties, such as ion exchange and sorption. Local chemical equilibria are affected by diffusion, advection, and electromigration. The program effort has extended the modeling to the pore walls. Near the waste-package boundary region there is, in effect, a titration occurring and a high pH is obtained. The high pH value invades the clay over a five-year period and then drops slowly. Clay resists the change in pH, the clay constituents acting as a buffer. The results of the modeling effort imply that (1) the high pH moves about 2-3 meters into the clay after 1000 years, (2) radionuclides will be released at the higher pH (more work is needed in this area), (3) edge effects of the repository do slow down the rate of change, indicating that smaller repository diameters may be more effective in containment, (4) the buffering capacity of the clay composition at 5 meters can drop the pH from 11.5 to 10 as opposed to any changes in plain water, and (5) there is a need to check the effect of calcite precipitation in the clay since the calcite then blocks the pores in the clay.

Session P7--Spent Fuel

P., Reed, D., "Detection and Speciation of Transuranic Elements Via Pulse Laser Excitation."

The long-term objective of these tests is to determine speciation in groundwater to supply input data for computer models. Presumably the identity and concentration of dissolved species could be determined at controlled temperatures, and also pH as well as other specified variables.

P.6.4., Reed, D. and Van Konynenburg, R. A., "Effect of Gamma Radiation on Moist Air Systems."

Donald Reed of Argonne National Laboratory spoke about experiments to be conducted regarding perturbation of the environment by pre-emplacement of waste canisters. The ambient temperature of the long-term moist air system at the proposed tuff site will rise and the environment will be exposed to gamma radiation levels in excess of 0.1 mrd/h. Determination of the effect of both of these perturbations on the gas phase is needed to fully characterize the environment of the waste package. Preliminary results of long-term modeling studies show that the formation of nitrate (NO_x) is a product of the gas-phase only, and is not found in aqueous solutions at the proposed site.

P.3.7., Gnirk, P., "State-of-the-Art Evaluation of Repository Sealing Materials and Techniques."

An invited paper detailing the status of current studies on several compositions of sealing materials, i.e. materials to seal fissures in rock disturbed by coring.

P.7.1., Werme, L. O., "Spent UO_2 Fuel Corrosion in Water; Release Mechanisms."

Lars O. Werme summarized work being done in Sweden on the release mechanisms of actinides due to corrosion of spent fuel in water. Tests were conducted on BWR fuel of three different megawatt-day/kilogram values, tested in groundwater and in deionized water. The amount of release was defined as the total of the amount dissolved, the amount adsorbed, and the amount in colloidal form. The work indicated that the release values had to be based on a centrifugate fraction since testing of membrane filters used resulted in values which were much too high. Apparently some of the uranium oxide fuel itself must be caught on the filters. The results show that strontium, which is dissolved in the fuel matrix, is preferentially leached from cracks and grain boundaries, indicating that there is alteration in the full matrix of the spent fuel. The Sr release is dependent only on time, not on redox conditions or any other factors. The leach vessel contents were found to be the same as the fuel.

P.7.2., Rawson, S. A., "The Effect of Waste Package Components on Radionuclides Released from Spent Fuel Under Hydrothermal Conditions."

Hydrothermal experiments to determine the effect of waste package components on the release of radionuclides were conducted in the Basalt Waste Isolation Project (BWIP). The results were reported by Shirley A. Rawson of Hanford Operations . The spent fuel tested was ATM 101, light water reactor fuel. The fuel was tested in basalt, in a low-carbon steel container, in a copper container, and in both containers with basalt-bentonite packing, under hydrothermal conditions using a slow-release period. The fuel was 99 percent UO_2, crushed and sieved (0.125-0.250 mm) for the experiment. Simulated Hanford Grand Ronde water was used, pH 9.75. In all experiments, matrix dissolution occurred, and there was preferential release of ^{14}C, ^{129}I, and ^{137}Cs as dissolved species. Cs, I, and C had time-invariant release in tests using only the steel or only the copper. In basalt only, Cs and C showed time-invariant release except at 300°C for C. In experiments using basalt with steel, the Cs, Sr, and C decreased with time, some below the point of detection. In tests with basalt and copper container, the Cs decreased, and the I, and C were time invariant. In all systems the presence of basalt decreases the release of C and Cs. All experiments showed less release over the 3-15 months duration than the maximum allowed by Federal regulations. During the tests, clay minerals formed in the basalt (K-feldspar in 300°C tests) and iron oxides and silicates formed with steel present.

P.7.3., Glasser, F. P., "Modelling Phase Distribution in Slag-Cement Blends and Their Solubility Properties."

A model has been developed that allows slag/cement ratios to be chosen to obtain minimum dissolution rates. Phases consisting of CaO, AL_2O_3, SiO_2, and MgO were identified and studied.

P.7.4., Sunder, S., Taylor, P., and Cramer, J. J., "XPS and XRD Studies of Uranium-Rich Minerals."

This paper deals with the mineralogical chemistry of very rich uranium deposits (12-55 wt% U) near Cigar Lake, Saskatchewan. An interesting comparison was made between the Cigar Lake deposit and a potential nuclear waste repository. This included data to indicate that the deposit had been stable for over a million years and was effectively isolated from the environment. The highest oxidation state of the U was U_3O_7. The authors' measurements indicate that the solubility of U is insignificant if the oxidation state is U_3O_7 or below. They conclude that geochemical conditions similar to Cigar Lake support the concept of deep burial of spent fuel.

Laboratory experiments show that the dissolution rate of uranium oxides increases with increasing oxidation state of the uranium, and have shown that below an oxidation of U_3O_7 dissolution is insignificant. Furthermore, this study included characterization of uranium oxide ores from the Cigar Lake deposit which revealed that these oxides are at an oxidation state of U_3O_7 or lower. The authors conclude that deep burial of nuclear waste, where oxygen is limited, is conductive to reduced uranium dissolution.

P.7.5., Wilson, C. N., "Summary of Results from the Series 2 and Series 3 NNWSI Bare Fuel Dissolution Tests."

C. N. Wilson of Westinghouse Hanford summarized the results of Series 2 and Series 3 NNWSI bare-fuel dissolution tests. The Series 2 tests are conducted in fused quartz vessels, not sealed, with chunks of oxidized fuel at 25°C. The Series 3 tests are conducted in sealed stainless steel vessels, at 25 and 85°C. The tests are semi-static, that is, liquid is sampled and then replenished so that the system approximates one in which there is a slow flow rate. J-13 well water is used. The tests show that the actinides saturate the solution, but Cs does not and often decreases with time. Uranophane was identified in the Series 3, 85°C tests. The data for ^{241}Am, and ^{239}Pu and 240 indicated that the levels meet EPA limits. $^{9}9Tc$, ^{137}Cs, ^{90}Sr, ^{14}C, and ^{129}I are preferentially released and the continuous Tc and Cs release is attributed to grain-boundary leaching.

P.7.6., Bruton, C. J., "Geochemical Modeling of Reactions Between a Spent Fuel Waste Form and J-13 Groundwater."

Carol Bruton of Lawrence Livermore National Laboratory explained geochemical modeling for reactions between spent-fuel waste and J-13 groundwater. The program simulates the chemical reactions in which C, Pu, Sr, Ca, U, and Si are dissolved into a static volume of water. The software calculates the amount of aqueous oxidized species and checks for saturation. If the water is supersaturated, then material is precipitated. If the water is not saturated, more material is dissolved, so that a saturated equilibrium situation is simulated. The assumption made is that the fuel is in a perforated container and that the groundwater has entered. Other assumptions are (1) there is congruent dissolution of the fuel, (2) the fuel dissolved into a fixed amount of J-13 at 25 and 90°C, (3) equilibrium with oxygen and carbon dioxide is maintained, (4) there is no inhibition of precipitation or dissolution, (5) all solids are potential precipitates, and (6) there are no materials interactions or radiolysis. The results show that U concentrations are low when silica is present. Many radionuclides are sequestered as oxides. As long as material is precipitated, amounts in solution are constant. No real difference is seen between the results of work at the two temperatures, and this lack may be an artifact of the thermodynamic database used in the modeling. At 90°C, the pH (which starts at 8.6) drops to 6.5, whereas the Eh rises from 0.58 to 0.74. Future work will include an isotope dilution method using the three isotopes of U to monitor the U in the leachant. The method uses measurable quantities to get the amount of fuel dissolved and to get the rate of dissolution.

Session P8--Glass Studies

P.8.1., Jantzen, C. M., "Pourbaix Diagram for the Presentation of Waste Glass Durability in Geologic Environments."

The first paper of the session, by Carol Jantzen, discussed the use of Pourbaix diagrams for the prediction of waste-glass durability in geologic environments. The waste glasses are rich in iron and during dissolution in aqueous environments nuclear waste-glasses have been observed to undergo active corrosion, passivation due to surface layer formation, and inactive corrosion or immunity. The factors to be considered with regard to glass durability are the effect of the glass composition, the solution pH, the solution Eh, silicon and boron loss due to release. When Pourbaix diagrams are drawn up for known data, pH, free energy, and mass loss versus Eh, all data are collinear. The dissolution of Si and B are found to be Eh dependent. The Fe in the glasses forms $Fe(OH)_3$ under oxidizing conditions, and $FeSiO_3$ under reducing conditions. In repository conditions due to the tuff, basalt, and bentonite, the glass will basically be in regions of passivation with regard to the groundwater.

P.8.2., Grambow, B., "Nuclear Waste Glass as a Long-Term Barrier for Radionuclide Release to the Environment."

The paper by B. Grambow of the Hahn-Meitner-Institute, Berlin, and colleagues in New Mexico and Stockholm, presented the results of modeling the performance assessment of COGEMA JSS-A glass using the GLASSOL model. The model predicts that release of the radionuclides will be complete at approximately 10^4 years, and that release of Fe, and Al is controlled by flow rate. The question of whether laboratory experiments can simulate repository environments and long-term processes in a reliable manner was assessed by comparison of laboratory results from field tests in the Stripa mine, Sweden, and by the use of natural glasses (i.e. basaltic glasses). In the model, the presence of bentonite has a minimal chemical effect on the durability of the glass. Grambow suggested that field tests and natural analogs should be used to verify the results of such modeling.

P.8.3., Feng, X., "A Model of Nuclear Waste Glass Dissolution Derived from Structural and Thermodynamic Properties of Constituent Oxides."

Xiangdong Feng of Catholic University presented a model of glass dissolution based on the structural and thermodynamic properties of the constituent oxides. This model is a variation of the Jantzen-Plodinec model. The basic assumption in Feng's model is that the metal-oxygen bond strength controls the durability and the viscosity. The more durable glasses have the higher viscosities.

P.8.4., Vernaz, E. Y., "Temperature Dependance of Nuclear Waste Glass Alteration Mechanisms."

A paper by E. Y. Vernaz of CEA, CEN/Valrho, discussed the temperature dependence of waste glass alteration mechanisms. The effect of long-term corrosion of glasses is difficult to simulate in the laboratory, but high-temperature testing may permit valid predictions of long-term behavior. If each mechanism of the leaching and dissolution of the glass can be identified separately, the results of static leaching tests may be useful if the data are extrapolated carefully. Those tests performed so far indicate that the secondary mineral phases formed do not seem to be rate controlling.

P.8.5., Tsukamoto, M., "Leaching of ^{241}Am from a Radioactive Waste Glass Corroded in the Presence of Stainless Steel Corrosion Products and/or Bentonite."

Masaki Tsukamoto of the Central Research Institute of the Electric Power Industry, Japan, and Swedish colleagues have studied the leaching of ^{241}Am from waste glass in the presence of stainless steel corrosion products and/or bentonite. The tests show that the Am is released to a greater extent in the presence of the corrosion products and bentonite than in the presence of bentonite alone. This greater release is true for other radionuclides, also. The general results of the testing are (1) ^{241}Am is strongly adsorbed on bentonite, (2) total release is low in the tests conducted, (3) the mass loss increases with the corrosion time, and (4) in general, ^{241}Am release in the repository may be very low compared to the total mass loss.

P.8.6., Lutze, W., "Chemical Durability of Cogema Glass R717 in High Saline Brines."

W. Lutze of the Hahn-Meitner-Institute, Berlin, discussed the chemical durability of COGEMA glass R717 in high-saline brine. The tests conducted are pertinent to the conditions in the salt dome being explored for a repository in the FRG and the effect of those conditions on borosilicate waste glass. The results of tests at 190°C when plotted on log-log scales as mass loss versus time show that there is a silica saturation point after which the loss of silicon is constant. Until that point is reached, the mass loss of silicon and boron from the glass is about equal. The dissolution reaction is not concentration dependent once the silica saturation point is reached. A plot of corrosion depth versus time shows no concentration dependence, but there is a dependence on transport. For high-magnesium brine and other high-saline brines, the forward rate reaction at 190°C is a linear time function and the rate decreases greatly with lower temperature.

P.8.7., Bibler, N. E., "Leaching ^{99}Tc From SRP Glass in Simulated Tuff and Salt Groundwaters."

The results of tests of leaching of ^{99}Tc from SRP borosilicate glass in simulated tuff and salt groundwaters were presented by N. E. Bibler of the Savannah River Laboratory. Leaching of ^{99}Tc was compared to the leaching of other elements in the glass and the effect of oxidizing and reducing conditions was compared. To obtain glass containing Tc, SRL black frit was doped with NH_4TcO_4 at 1150°C. It was found that the Tc was very volatile, from 50-75 percent having been lost from the melt. Static leaching tests were conducted in WIPP brine A and in J-13 tuff groundwater. In all tests the pH rose. In brine, the Tc leached congruently with the silicon, but in the J-13 water the Tc leached congruently with the boron. In reducing conditions in J-13 water the pH increased to very high values and the glass dissolved to a great extent. Mass loss was high. Normalized mass loss for Tc was low, however.

P.8.8., McGrail, B. P., "Modeling the Dissolution Behavior of Defense Waste Glass in a Salt Repository Environment."

Modeling of the dissolution of SRL-165 defense waste glass in a salt repository was discussed by B. P. McGrail of Pacific Northwest Laboratory. The MASSBAL software postulates rate loss for silica and formulates simplified mass balances. Other codes apply geochemical features but are limited in usefulness because of present limitations in thermodynamic databases. The MASSBAL model was applied to dissolution in brine under oxidizing conditions. The effect of metal corrosion on the solubility of ^{239}Pu was studied. In steel containers as corrosion occurs, when all the iron is fully oxidized, the Pu solubility rises sharply due to the presence of the container reaction products. It was found that the model and experimental results agree well. The precipitates that form in experiments depend on the metal/glass surface are a ratio, and this fact should help govern individual container sizes.

P.8.9., Bruton, C. J., "Geochemical Simulation of Dissolution of West Valley and DWPF Glasses."

Carol Bruton of Lawrence Livermore National Laboratory spoke about geochemical simulation of dissolution of West Valley and DWPF glasses. See her paper in Session P7 for information about the EQ3/6 software used in the modeling. In modeling using the two different glasses, it was found that dissolution in J-13 gave very similar results. The major conclusions are that: (1) radionuclides tend to be sequestered by oxides, hydroxides, and silicates, (2) solid precipitates limit the radionuclide concentration in solution, (3) equilibrium with the solid phases need not fix the concentration in solution, and (4) release rates of actinides are decreased as the redox potential decreases.

P.8.10., Bidoglio, G., "Influence of Groundwater on Glass Leaching and Actinide Speciation."

In a paper on leaching studies, G. Bidoglio of the Joint Research Centre, CEC, reported on the influence of the groundwater composition on glass leaching and actinide speciation. Experiments were performed on borosilicate glasses with actinides in both bicarbonate groundwater with a pH of 8.3 and salt brine with a pH of about 6 under both oxidizing and reducing conditions. Under oxidizing conditions in the bicarbonate water, the Pu release rates were lower than those of Np. In the brine under oxidizing conditions a steady-state release rate was achieved. In reducing conditions, the initial release rate was high and decreased at first and then increased. The decreasing release rate was related to a decreasing redox potential. The leachate chemistry was found to be dependent on colloid formation, tying up the Pu in the suspended particulate matter.

P.8.11., Van Iseghem, P., "Results from the Long-Term Interaction and Modelling of Two Simulated Belgian Reference High Level Waste Glasses."

P. Van Iseghem of the S.C.K./C.E.N in Belgium reported results from the long-term interaction and modeling of two simulated Belgian reference high-level waste glasses. One of the glasses had a high alumina content. Leaching experiments had been conducted in distilled water at 90°C. Then modeling was performed using PHREEQUE and GLASSOL codes. For the high-alumina glass there was an indication of some long-term leaching. Comparison of the results indicates that the GLASSOL model fits best.

P.8.12., Lutze, W., "Chemical Corrosion of Lead-Iron Phosphate Glass."

The chemical corrosion of lead-iron phosphate glass was discussed by W. Lutze of the Hahn-Meitner-Institute, Berlin. The glass contains better than 6 percent LWR waste. In soxlet experiments, it was found that the lead has a low leach rate and decreases with time in comparison with the borosilicate leach rate which remains relatively constant in similar experiments. The phosphate glass is more durable in comparison with borosilicate glass. When leach data for P, Pb, and Cs are plotted, it is found that there is congruent dissolution in the beginning, and then the dissolution drops off and continues at a low rate. The presence of iron has no real effect. In borosilicate glass, the dissolution rate decreases when silicon saturation is reached and the soluble species is B. In the phosphate glass, the dissolution rate decreases when the P and Pb saturation is reached and the soluble species is Cs.

Session P9--Corrosion Studies

P.9.1., Bates, J. K., "Methods to Evaluate the Long-Term Performance of Waste Package Interactions."

Although this paper was given in the symposium session on corrosion studies, since points were made which reoccurred throughout the symposium, this paper might have been more appropriately presented first. In modeling, first principles must be combined with empiricism, but with a firm foundation included for the empiricism. It is absolutely necessary to use correct data in modeling and, therefore, the data must be evaluated before insertion into the model. One must relate the experiments to the repository and relate the models to available laboratory analogues.

Bates was very emphatic in pointing out that experimental data must be obtained and evaluated before any modeling efforts can be attempted. He expressed concern at the proliferation of models now being developed in the absence of data. Once a model is developed, however, it must then be verified as realistic on the basis of experimental and field observations.

P.9.2., Brehm, W. F., "Container Corrosion in the Post Closure Period of a Repository in Basalt."

Brehm obtained corrosion data on steel, copper, and a copper-nickel alloy in autoclaves at elevated temperature and pressure. The data indicate that at 300°C the corrosion rate of steel is high, but decreases with time at a parabolic rate. The corrosion rate of copper is linear with time under these same conditions, and the copper-nickel alloy displays a nonlinear, rapidly increasing corrosion rate in the same 28-month period. Preliminary conclusions indicate that packing material does not affect the corrosion rate of steel, but increases the corrosion of copper. In all cases, the corrosion rates are low.

P.9.3., Haberman, J. H., "Corrosion Studies of a Waste Package Material in Salt Repository Relevant Hydrothermal Brines."

Measurements made over a 6-month period indicate that the corrosion of A216 steel is 50 times greater in inclusion brine than it is in dissolution brine. Furthermore, the corrosion of steel in inclusion brine at 200°C (approximately 6 mm/y) is several times greater than that at 100°C.

P.9.4., Van Orden, A., "The Archaeological Data Base Relevant to Long-Term Corrosion Behavior of A-216 Mild Steel."

This study of Roman nails recovered from archaeological sites, reveals that after almost 2000 years, much of the steel is not oxidized; however, the examination indicates that pitting attack is a common occurrence on this ancient steel. The composition of these nails is similar to that of A-216 steel.

P.9.5., Goodwin, F. E., "Corrosion of Lead and Lead Alloys in Simulated Repository Environments."

This study reports the results of an 18 month corrosion study of Pb in simulated repository conditions, and indicates that the corrosion of lead in a simulated tuff environment is almost 10 times greater than that in basalt or salt.

P.9.6., Bullen, D., "Impact of Phase Stability on the Corrosion Behavior of the Austenitic Candidate Materials for NNWSI."

This study indicates that, at repository temperatures of less than 250°C, carbide precipitation in austenitic stainless steels will occur in approximately 50 years. The conclusions indicate that (1) carbide formation is limited, (2) intermetallics will not form, and (3) the phase stability of 825 is superior to that of 304 and 316.

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