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

January 15, 1987

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PDR  
 LPDR

Mr. Everett A. Wick  
 Division of Waste Management  
 Office of Nuclear Materials Safety and Safeguards  
 U.S. Nuclear Regulatory Commission  
 Washington, DC 20555

Distribution:  
*X WICK*  
 (Return to WM, 623-SS)

*X Jean Tillet*

Re: Monthly Letter Status Report for December 1986 (FIN-A-4171-6)

Dear Mr. Wick:

Enclosed is the December 1986 monthly progress report for the project "Evaluation and Compilation of DOE Waste Package Test Data" (FIN-A-4171-6). The financial information is reported separately.

Sincerely,

*Charles G. Interrante*

Charles G. Interrante  
 Program Manager  
 Corrosion Group  
 Metallurgy Division

Enclosures

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Monthly Letter Report for December, 1986

Published January 1987

(FIN-A-4171-6)

Performing Organization: National Bureau of Standards  
Gaithersburg, MD 20899

Sponsor: Nuclear Regulatory Commission  
Office of Nuclear Materials Safety and Safeguards  
Silver Spring, MD 20910

**TASK 1 -- Review of Waste Package Data Base**

Status Report on the Database for Reviews and Evaluations on HLW Data

**Status of HLW Database**

Four of the five files necessary for implementation of the HLW Database have been completed and have been loaded into the IBM AT. These files are: Reviews (REV), Abstracts (ABS), Figures (FIGS), and Key words (KEY). Due to the number of revisions in the review form, the file Review Form (REV) will require additional development. During the month of December, the key words were converted to files and loaded in the database. Thirty-one items (technical reports, books, and journal articles) have been entered into the database. Some of these materials will be reviewed, however, the database will include many more items than those reviewed. This initial data entry has necessitated many decisions and some changes to the file structure. Documentation is being written concurrently with database development.

**Status of the Automated Tracking System**

An automated tracking system has been developed for tracking each NBS review as it passes through the review cycle. Bibliographic information from the main database is used in this system; therefore, it needs to be keyed into the total system only once.

**Projected Delivery of HLW Database**

Both the HLW database and the Tracking System will require changes as these systems become fully operational and real data are entered. The time needed for full implementation is estimated to be three months from now. A target date of March 1, 1987, has been set for the first database tape to be delivered to the NRC. It will include all NBS reviews completed and WERB approved as of February 20, 1987. The database will be menu driven so that it can be easily searched.

Appended to this report are copies of the following three Draft Reviews not previously submitted. Comments by NRC and its contractors are solicited.

1. HEDL-7612, "Corrosion of Copper-Based Materials in Gamma Radiation," June 1986
2. B036177, "Analysis of the Effects of Radiation on the Chemical Environment of a Waste Package in a Nuclear Waste Repository in Basalt," March 1984
3. RHO-BW-SA-280 P, "Conceptual Design of a Waste Package for Emplacement in Basalt," February 1983

SRP -- Review has been initiated on the following report this month.

1. BMI/ONWI-626, "ERG Review of the SRP Salt Irradiation Effects Program," November 1986

SRP -- Review is continuing on the following report.

1. BNL 32001, "Very Rough Preliminary Estimate of the Colloidal Sodium Induced in Rock Salt by Radioactive Waste Canister Radiation," by P.W. Levy and J.A. Kierstead, September 1984

BWIP -- Review is continuing on the following reports.

1. RHO-BW-SA-391P, "Effect of Grande Ronde Basalt Groundwater Composition and Temperature on the Corrosion of Low-Carbon Steel in the Presence of Basalt-Packing," August 1985
2. SD-BWI-DP-060, "Interim Data Document for the Advanced Conceptual Design of High-Level Waste Packages for a Repository in Basalt," November 1984
3. RHO-BW-SA-316, "Irradiation-Corrosion Evaluation of Metals for Nuclear Waste Package Applications in Grande Ronde Basalt Groundwater," November 1983
4. SD-BWI-TI-235 (B032012), "Corrosion Evaluation of Candidate Iron-Based Nuclear Waste Package Alloys in Grande Ronde Basalt Groundwater," February 1984

NNWSI -- Review has been initiated on the following report.

1. UCRL-15723, "NNWSI Waste Form Test Method for Unsaturated Disposal Conditions," March 1985

NNWSI -- Review is continuing on the following reports.

1. NUREG/CR-4619, "Stress Corrosion Cracking Test on High-Level-Waste Container Materials in Simulated Tuff Repository Environments," June 1986

2. UCRL-15825, "The Effect of Gamma Radiation on Groundwater Chemistry and Glass Leaching as Related to the NNWSI Repository Site," May 1986
3. ANL-85-41, "One-Year Results of the NNWSI Unsaturated Test Procedure: SRL 165 Glass Application," August 1984
4. MRB-0418/UCID-20172, "Attachment 10, Potential Corrosion and Degradation Mechanisms of Zircaloy Cladding..in a Tuff Repository"
5. HEDL-7546, "C-Ring Stress Corrosion Cracking Scoping Experiment for Zircaloy Spent Fuel Cladding," March 1986
6. HEDL-7545, "Zircaloy Spent Fuel Cladding Electrochemical Corrosion Experiment at 170 C and 120 psiA H2O," April 1986

MCC -- Review has been initiated on the following report.

1. "Aging of Cast Duplex Stainless Steels in LWR Systems", O. K. Chopra and H.M. Chung, Nuclear Engineering Design, 89, 305-318 (1985).

**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.

Two NBS proposals for Laboratory Testing to confirm the accuracy of DOE data have been approved by NRC, as follows:

1. Pitting Corrosion of Steel Used for Nuclear Waste Storage
2. Corrosion Behavior of Zircaloy Fuel Cladding

**TASK 4 -- General Technical Assistance**

NBS was represented at the MRS 87 meeting in Boston, MA, December 1-6, 1986 by Dr. U. Bertocci, Dr. A. Fraker, Dr. C. Interrante, and Dr. E. Plante. A trip report is attached.

NBS was represented at the NRC and DOE Technical Meeting on DWPF Vitrification Process, Waste Form and Supporting Data Base held on December 9 and 10, 1986 in Washington, DC by Dr. C. Interrante, Dr. M. Linzer, Dr. E. Plante, and Ms. J. Ruspi.

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

DATE SOURCE

(a) Organization Producing Data

Hanford Engineering Development Laboratory, Operated by Westinghouse  
Hanford Company, PO Box 1970, Richland, WA 99352

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

W. H. Yunker, "Corrosion of Copper-Based Materials in Gamma  
Radiation," HEDL-7612

DATE REVIEWED: 10/7/86

TYPE OF DATA

Experimental, corrosion, SCC, crevice corrosion

MATERIALS/COMPONENTS

Pure Cu (CDA 101), 7% Al bronze (CDA 613), 30% Ni-Cu (CDA 715)

TEST CONDITIONS

Three types of specimens: flat samples, bent strips for SCC, crevice  
specimens. Environment: water vapor-air at 95°C and 150°C, and immersed  
in J-13 water at 95°C. Gamma radiation field of 10<sup>5</sup>R/h. Exposure: 1, 3  
and 6 months

METHODS OF DATA COLLECTION/ANALYSIS

Changes in chemical composition of gas and water.  
Weight changes, oxide film weights, visual examination.  
Chemical composition of oxide films by Auger electron spectroscopy  
and x-ray diffraction.  
Dye-penetiant tests for SCC.

AMOUNT OF DATA

18 figures: 9 are drawings or photographs of the assembly and specimens.

- 1) Gamma flux (0 to 5.5 x 10<sup>-5</sup> R/h) vs. position from top of irradiation  
tube specimens (0 to 0.6 m)
- 2) Vessel gas pressure (0-300KPa) vs. time up to 115 days

Corrosion data on axes of 1 to 100 mg,  $10^2$  to  $10^3$  h:

- 1) log weight loss (mg) vs. log time (h) for CDA 101
- 2) log weight loss (mg) vs. log time (h) for CDA 613
- 3) log weight loss (mg) vs. log time (h) for CDA 715

Four Graphs are composition profiles of the surface film vs. sputter time from Auger data, two for CDA 613 and two for CDA 715.

- 14 Tables:
- 1) Number of specimens exposed (254)
  - 2) J-13 water composition
  - 3) Estimated  $\gamma$ -Dose rates for various kinds of waste
  - 4) Composition of specimens
  - 5) Data logger input channels
  - 6) Example of data report
  - 7-8) Gas composition
  - 9) Water composition in vessel T-1 at 95°C
  - 10) Water Composition
  - 11) Auger analyses for CDA 101, 613 and 715
  - 12) X-ray diffraction results
  - 13) Uniform corrosion data
  - 14) Stoichiometry of Cu oxide on CDA 101

Appendix: Results of visual examination of weight loss and bend specimens after oxide film removal.

#### UNCERTAINTIES IN DATA

No statistical analyses of the results

#### DEFICIENCIES/LIMITATIONS IN DATABASE

Data are considered preliminary. Longer exposure times are currently in progress.

#### KEYWORDS

Copper, copper alloys, corrosion, SCC, crevice corrosion,  $\gamma$ -field

#### COMMENTS

Results indicate that pure copper (CDA 101) has less tendency to localized attack when compared with the alloys tested and that the 7%-Al Bronze (CDA 613) shows lower uniform attack. The presence of liquid on the surface enhances corrosion. (CDA 715) a significant enhancement of corrosion with  $\gamma$ -ray exposure was found only for the 30% Ni-Cu alloy. No cracking was observed.

APPLICABILITY OF DATA TO LICENSING

[Ranking: key data ( ), support (X)]

(a) Relationship to Waste Package Performance Issues Already Identified

This document addresses issue 2.2.4.2 (what is the effect of radiation on the corrosion behavior of the waste package container). Particular emphasis in the document is devoted to radiation effects on localized modes of corrosion.

(b) New Licensing Issues

(c) General Comments

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

DATA SOURCE

(a) Organization Producing Data

Pacific Northwest Laboratory, Richland, Washington 99352

(b) Author(s), Reference, Reference Availability: Gray, W. J.,

"Analysis of the Effects of Radiation on the Chemical Environment of a Waste Package in a Nuclear Waste Repository in Basalt", March (1984).

DATE REVIEWED: October 28, 1986

TYPE OF DATA

Experimental data on the effects of gamma and alpha radiation on simulated Grande Ronde basalt groundwater. Some computer calculations on the radiolysis of methane are made but the major emphasis is on an experimental approach.

MATERIALS/COMPONENTS

Simulated basalt groundwater. Some experiments included the presence of basalt and/or bentonite. To simulate the composition of basalt groundwater, which contains up to 700 mg/l of methane at 25°C, samples were pressurized under gaseous N<sub>2</sub> and CH<sub>4</sub>.

TEST CONDITIONS

The simulated basalt ground water was placed in stainless steel vessels with quartz liners and pressurized to about 0.14 MPa with gaseous N<sub>2</sub> and 3.30 MPa with gaseous CH<sub>4</sub>. Gamma irradiation was done in a <sup>60</sup>Co facility at dose rates of 2x10<sup>4</sup> to 5x10<sup>6</sup> rad/hr. Alpha irradiation was done by spiking the solutions with <sup>238</sup>Pu at a concentration of 4x10<sup>-4</sup> M resulting in a dose rate of 2x10<sup>4</sup> rad/hr. The Pu concentration exceeds the solubility in the simulated groundwater at a pH above 3 so the solutions were stirred to provide uniform alpha exposure. The volume ratio of liquid to gas was about 4/1. For the gamma irradiation about 3/4 of the gas volume was exposed to the high radiation field. For the alpha irradiation, only the liquid phase was irradiated.

METHODS OF DATA COLLECTION/ANALYSIS

Gases were analyzed by mass spectrometry. Analysis methods for liquids included Inductively Coupled Plasma (ICP) spectroscopy for cations and carbon analysis for organic and inorganic carbon. Solids were analyzed by Fourier Transform Infrared spectrometry. Gel Permeation Chromatography was used to establish molecular weight distribution of the polymeric radiolysis products. Elemental fractions of C, H, and O were determined with an elemental analyzer.

### AMOUNT OF DATA

Tables: Composition of Synthetic Grand Ronde Basalt Groundwater; Solution Concentrations used in Radiolysis Experiments; Composition of Water Used in Irradiation Tests; Irradiation Conditions and Post-Irradiation Analysis Performed; Irradiation Conditions and Gas Compositions of Irradiated Samples; Concentrations of Cations Found in Irradiated Solutions; Analytical Results from some of the Gamma Irradiation Tests; Gas Concentrations and Total Pressure Predicted at Total Dose Rate of 46 Mrad (Dose rate was 1.5 Mrad/hr); Gas Concentration and Total Pressure at Total Dose of 77 Mrad (Dose rate was 1.1 Mrad/hr).

Figures: IR Absorption Spectra for Tests 45 and 50; Gas Pressures Resulting from the Radiolytic Decomposition of Methane, Gas Pressure ( $10^{-4}$  to 100 Atm) vs Time (1 to  $10^5$  Sec) based on computer model.

### UNCERTAINTIES IN DATA

Not dealt with except to note that deviant measurements are thought to result from mistakes in procedure.

### DEFICIENCIES/LIMITATIONS IN DATABASE

There is some evidence that Si was leached from the quartz inserts during the radiolysis measurements.

### KEY WORDS

alpha radiation, basalt, basic solution, bentonite, computer calculation, data analysis, experimental data, gamma radiation, high pressure, high temperature, laboratory, simulated basalt groundwater, radiolysis of basalt groundwater.

### GENERAL COMMENTS

The radiolysis of basalt groundwater, which has a high concentration (up to 700 mg/l at 25°C) of CH<sub>4</sub> (methane) by alpha and gamma radiation results in the formation of higher molecular weight organic substances. Average molecular weights of the organic fractions vary from 100 to 50,000 and average from 2,000 to 3,000. The original intent of this work was to develop and use computer modeling to calculate concentrations of radiolytic products and performing only a few laboratory measurements to make adjustments in the model. However, because of the complexity of the process, many reaction rate constants are not known, so more emphasis has been placed on laboratory measurements. The primary concern has been to identify and characterize the higher molecular weight products which it is hoped may serve as absorption sites for leachate radionuclides. But, the report emphasizes that experimental problems caused by Si contamination may have affected some of the results. No effort is made in this report to relate the results to possible effects in a repository. The report suggests that this will be a future objective.

APPLICABILITY OF DATA TO LICENSING:

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

- (a) Relationship to Waste Package Performance Issues Already Identified  
This report provides supporting data for issue 2.1.3.1 regarding how radiolysis effects the chemical nature of the groundwater reaching the waste package container and for issue 2.3.5 regarding how the release rate of radionuclides is likely to be affected by radiation.
- (b) New Licensing Issues
- (c) General Comments

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

DATA SOURCE

(a) Organization Producing Report

Rockwell Hanford Operations, Energy Systems Group, Richland,  
Washington.

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

W.J. Anderson, "Conceptual Design of a Waste Package for  
Emplacement in Basalt," RHO-BW-SA-280 P, February 1983.

DATE REVIEWED: 14 October 1986

TYPE OF DATA

(1) Scope of the Report

The report is a reevaluation of Basalt Waste Isolation Project (BWIP) waste-package conceptual designs based on revisions of the environmental conditions to be expected in the repository.

(2) Failure Mode or Phenomenon Studied

An earlier six-component waste-package design resulted from unrealistic assumptions about the waste-package environment. First, the bentonite/basalt backfill was originally expected to become saturated with water and swell, thereby filling the void space between an overpack and the host rock. The swelling pressure was expected to grasp the waste-package assembly and prevent easy retrieval. Therefore, a mullite sleeve was included in the original design to prevent this swelling backfill from clamping the overpack. However, subsequent examination of the backfill temperature and atmospheric pressure expected to exist between the time of waste emplacement and retrieval operations has shown that the assumed backfill saturation and swelling cannot occur prior to permanent closure of the repository.

Second, the original assumption was that high-oxygen groundwater would be in contact with the overpack throughout its life. Therefore, a material resistant to corrosion in such groundwater would be needed and the original design called for a titanium alloy overpack. Further evaluation and materials testing indicated that contact between the waste container and high-oxygen groundwater will be limited to, at most, a matter of only days or weeks after permanent closure of the repository. During this period, corrosion of a carbon-steel overpack would be insignificant in relation to the thickness of the material required for structural adequacy. The corrosion allowance for canister/overpack materials should be based on low-oxygen groundwater conditions. The presence of basalt gives rise to low-oxygen in the groundwater.

MATERIALS/COMPONENTS

The early waste-package designs provided for a six-component package consisting of (1) a perforated aluminum borehole liner which surrounded (2) compressed blocks of sodium bentonite/basalt backfill, which, in turn, surrounded (3) a mullite retrieval sleeve. In addition, there was (4) a titanium alloy overpack containing (5) a carbon-steel canister of waste, with (6) graphite buffer material between the overpack and the canister. The temperatures, pressures, and chemistry of the groundwater of the proposed repositories are reexamined in this report.

The materials proposed for the new simplified waste-package conceptual design include stainless steel canisters for commercial high-level waste, carbon-steel canisters for spent fuel rods from pressurized water reactors or boiling water reactors, and a backfill consisting of 75% crushed basalt/25% sodium bentonite.

Because the site is not expected to fill with groundwater and establish hydrostatic pressure until after permanent closure, the need for the mullite retrieval sleeve is eliminated. The Eh of the groundwater in contact with the canister will be controlled by crushed basalt in the backfill thereby limiting corrosion and the solubility of radionuclides and eliminating the need for a buffer material and titanium alloy overpack. Alternate designs are referred to in the report. Changes in the positioning of the waste packages from a vertical to a horizontal orientation are also indicated in drawings of the new design.

TEST CONDITIONS

## (1) State of the Material being Tested

Not applicable to this report.

## (2) Specimen Preparation

Not applicable to this report.

## (3) Environment of the Material being Tested

The report reviews the design values for pressure, temperature, and groundwater composition for the basalt repository. The design value for external pressure on the canister prior to closing is 0.15 MPa. The waste package storage boreholes are not sealed from the access tunnels in order to permit ventilation for operating personnel. After permanent closure, groundwater seeping into the backfill will pressurize the void between the borehole wall and the canister. The pressure on the waste canisters will rise until it reaches the ambient hydrostatic pressure, which is the design pressure used after permanent closure. The relationship between repository depth and hydrostatic pressure at the Hanford Site is given by:

$$\text{Pressure (MPa)} = 0.063 + 0.00979 \text{ Depth (meters)}$$

<u>Repository</u>	<u>Depth</u>	<u>Design Pressure</u>
Umtanum basalt flow	1,128 m	11.1 MPa
Middle Sentinel Bluffs basalt flow	945 m	9.3 MPa

The ambient temperature of the host rock used for design is based upon repository depth:

$$\text{Temperature } (^{\circ}\text{C}) = 14.83 + 0.038 \text{ Depth (meters)}$$

<u>Repository</u>	<u>Depth</u>	<u>Ambient Temp.</u>
Umtanum basalt flow	1,128 m	58 °C
Middle Sentinel Bluffs Basalt flow	945 m	51 C

Soon after emplacement of the waste, temperatures at the borehole surface exceed 100 °C due to the decay heat of the radioactive waste. Groundwater seeping in before closure will vaporize quickly and displace the air in the boreholes with water vapor in a day or two. The temperature will continue to rise, reaching a peak of 235 °C between 5 and 10 years after emplacement for commercial HLW from processed spent fuel. At the time of permanent closure, the rock temperature will decrease to the range of from 170 to 200 °C. Vaporization caused at these temperatures should prevent contact between the canister material and liquid groundwater until after permanent closure. After closure, the temperature will continue to decrease reaching 100 °C in about 400 years. At that time, the heat generation rate of the waste will be sufficiently low that the waste temperature will be within 5 °C of the borehole surface temperature.

Groundwater composition in the Grande Ronde basalt flows is of low ionic strength (about 20 milliequivalent total cations plus anions). Sodium is the dominant cation, with varying amounts of minor cations, potassium, calcium, and magnesium. The chemically dominant anions are chloride and sulfate, and also a relatively high fluoride content compared to potable water. Dissolved silica in groundwater in contact with basalt follows a solubility limit for amorphous silica as a function of temperature. The chemical behavior of the groundwater is characteristic of that for either sodium chloride or sodium chloride - sodium sulfate solutions.

Tests of the groundwater chemistry indicate that the ambient Eh and pH conditions favor limiting the solubility and, therefore, the transport of many radionuclides. At basalt temperatures of 58 and 300 °C, the groundwater pH is nominally 9.4 and 7.8, respectively. Results of hydrothermal tests show that reaction between basalt and groundwater to remove dissolved oxygen occurs rapidly. In tests at 150 °C and 300 bars, the dissolved oxygen content of simulated groundwater in contact with crushed basalt decreased from 8.5 mg/l to 0.4 mg/l in 190 hours. Reasonable extrapolation of the available data indicates that the dissolved oxygen would be  $<10^{-3}$  mg/l in about 600 hours. Other data indicate that the Eh of groundwater in the repository near field will return to the Eh of ambient Grande Ronde basalt groundwater in a few months after permanent closure.

#### METHODS OF DATA COLLECTION/ANALYSIS

This report is a review of the BWIP waste-package design as of March 1983. It provides some of the repository characteristics (e.g. temperature and pressure) as well as calculated results for time-temperature relationships in the repository which are needed for evaluating the choice of container

It provides some of the repository characteristics (e.g. temperature and pressure) as well as calculated results for time-temperature relationships in the repository which are needed for evaluating the choice of container materials in the future. The review of the site-specific conditions for the basalt repository permits the design of a simplified waste package.

#### AMOUNT OF DATA

There are three figures. Figure 1, titled "Early NWRB Waste Package Emplacement Concept," is a diagram of the original waste package design. Figure 2 gives temperature estimates for the emplacement borehole surface over time for HLW from processed spent fuel. It is titled "Commercial High-Level Waste Package Temperature Estimates," and has a temperature scale from 50 to 400 °C and a time scale from 10<sup>0</sup> to 10<sup>4</sup> years. Figure 3, titled "The NWRB Reference Commercial High-Level Waste Package Conceptual Design," is a diagram of the revised waste package design.

There are two tables. Table 1, titled "Waste Package Dimensions - Conceptual Design," gives dimensions for the carbon steel canister, backfill thickness and borehole diameter for three types of waste. Table 2, titled "Waste Package and Excavation Costs," lists the estimated costs for the parts of the waste package and the excavation for four designs and compares the totals for each design.

#### UNCERTAINTIES IN DATA

Not given by the author.

#### DEFICIENCIES/LIMITATIONS IN DATABASE

Not given by the author.

#### KEY WORDS

conceptual design, bentonite, basalt, stainless steel canisters, carbon steel canisters, Grande Ronde basalt

#### GENERAL COMMENTS

#### RELATED HLW REPORTS

These reports are cited in the bibliography.

RHO-BWI-LD-23  
RHO-BW-ST-25 P  
DOE/RL 82-3  
RHO-BW-CR-136 P/AESD-TME-3142

#### APPLICABILITY OF DATA TO LICENSING

No specific issues are addressed here.

## Report - 1986 Fall Meeting of the Materials Research Society

### Symposium L: Scientific Basis for Nuclear Waste Management X.

This symposium was held on Dec. 1 through Dec. 4, 1986 in Boston MA, and proceedings will be published as Volume 84 of the Materials Research Society Symposia Proceeding Series. The symposium received support from both the Department of Energy and the Nuclear Regulatory Commission. An estimate of the cumulative attendance over the four days would be 200 to 300 attendees. The Symposium consisted of eight sessions of oral presentations and eight poster sessions. The papers covered many areas of nuclear waste disposal which currently are thought to be important. NBS participated in the meeting as attendees (A. C. Fraker and E. Plante), session chairman (C. G. Interrante), author and presenter of a paper (U. Bertocci). J. Fong presented an invited paper. It is anticipated that the publication of the proceedings of the MRS-87 Symposium on Scientific Bases for Nuclear Waste Management will be available in March 1987. This tentative date may be met due to the fine efforts of J. Bates and W. Seefeld of Argonne National Laboratory, who planned to have edited and sent camera-ready copy to the publisher by January 1, 1987.

The symposium covered a wide area from statistics to corrosion science, and from inorganic chemistry and geochemistry to mechanical engineering, so the typical attendee was not conversant with all of the subjects. A significant part of the content of the papers was hardly new; for instance the work presented on corrosion of copper-base alloys was essentially identical to that presented in Houston last spring.

It was interesting to hear some of the work being carried out in foreign countries, notably Germany, Sweden, Canada, Finland, France and the United Kingdom and others. For example, the modeling work done at Harwell by G.P. Marsh, S. M. Sharland and coworkers is raising some important points concerning the extent of localized corrosion which can be expected in repository conditions. Meeting with the authors and hearing their presentations was very informative. Much work has been done and much more is needed to solve the problems associated with understanding the waste package. The session topics and brief discussions are presented as follow and will direct the reader to the author or the published paper.

#### Session L1 - Plenary Session on Long Term Projection of Materials Interactions

Considerations for licensing and for extrapolating tests for long term projections were presented by T. C. Johnson, K. Chang, T. L. Jungling, L. S. Person, C. H. Peterson, J. Vogelwede and E. Wick of the Div. of Waste Management, Nuclear Regulatory Commission, Washington, DC. Other aspects of long term waste disposal, including materials performance, validation of models, nuclear waste glass, repository material interactions, natural analogues for predicting corrosion of borosilicate glass and radiation effects in ceramics, were discussed in four other talks of this session, and J. Fong of the National Bureau of Standards discussed database strategy for engineering decision making. He defined a global database and spoke to the importance of judgement on the part of the engineers who must use the database. When the database is insufficient, due to limitations in time and

money, good engineering judgement must be used in most important decisions affecting the public.

#### Session L2 - Waste Form Performance: Spent Fuel

V. M. Oversby talked about the requirements of the EPA and NRC and the calculations needed to assure required radionuclide containment for 10,000 years. Knowledge of waste form performance and of the acting physical and chemical processes are needed to make these calculations. Much of her talk was collected from previous NNWSI publications. Another paper, by J. J. Mahoney, reported on behavior of spent fuel in a simulated basalt repository environment and found that actinide release was reduced in the presence of basalt (This could be due to experimental design.) and that U concentration may be controlled by solubility. Other papers (S. Sunder, et.al. and H. Christensen) reported on the oxidation of  $UO_2$  by alpha-radiolysis products and the retardation of this oxidation by reducing ions such as  $H_2$  or  $Fe^{2+}$ . C. N. Wilson reported on radionuclide release from spent fuel with various cladding defects in J-13 water. Transport analysis of radionuclide transport from holes in the canister was presented by P. L. Chambre, et.al.

#### Session L3 - Metal Corrosion

The papers in this session dealt with local and general corrosion. M. McNeil reviewed statistics of pitting, pit depths and distributions in carbon steel and related findings to repository conditions and needs for future experimental data. U. Bertocci, et.al. reported on the statistical analyses of passive current breakdown events decay rates to predict pitting initiation. D. Merz and M. Lewis presented three BWIP/MCC reference test procedures along with statistical treatment of data and of interlaboratory variation. The three tests discussed were the BWIP/MCC-105.5 Air/Steam Test, the BWIP/MCC-105.1 Static Pressure Vessel Test and the BWIP/MCC-105.4 Flowby Test. G. P. Marsh, et.al. of Harwell discussed localized and general corrosion of carbon steel containers for nuclear waste and concluded that localized corrosion would not occur if oxidizing conditions were not present.

Marsh, et al. also consider the long term corrosion of carbon steel containers for nuclear waste in a granitic repository. Under such conditions carbon steel may exhibit general, and localized corrosion or passive behavior depending on the exact composition and redox potential of the groundwater contacting the containers, localized corrosion being of most concern because it has the fastest propagation rate. It is well established, however, that such localized corrosion is only possible when the environment is sufficiently oxidizing to maintain a positive potential gradient between the cathodic surface and the corrosion sites, which requires that species with oxidizing potentials greater than water need to be present. This fact provides a basis for estimating the periods during which containers may be subject to localized and subsequently to general or passive corrosion, and hence for making an overall assessment of the metal allowance required for a specified container life. Such an analysis has been made in which the rate of consumption of oxygen and oxidizing radiolysis products is equated to the leakage current from a passive steel surface. It is concluded that localized corrosion is only possible for a small proportion of the required container life of 500-

1000 years. Thus, this work stresses that the form and rate of corrosion must be known over long times, using firm mechanistic understanding, without which local corrosion must be assumed and when this is done, an unacceptable conclusion is reached: unrealistically thick containers must be used. Hence, the kind of corrosion and its form are being investigated to permit general corrosion modeling.

S. G. Pitman's examination of stress corrosion cracking (SCC) susceptibility of cast mild steel found no tendency for SCC. However, there was some loss of ductility which indicates that this material and its resistance to SCC or other cracking mechanisms need further study. Under fatigue loading, he showed da/dn values could be higher (faster rate of crack growth) in brine than in air, indicating that corrosion fatigue values are conservative measures of crack extension rate.

Metal matrix studies reported by P. M. Mathew and P. A. Krueger were conducted on lead, zinc and aluminum-7%silicon. Lead showed almost no corrosion while the zinc and aluminum-7%silicon corroded and pitted.

#### Session L4 - Low Level Waste Materials

Papers in this session dealt with chemical aspects such as leaching (S. Hoyle and M. W. Grutzeck, and A. T. Jakubick, et. al.) and solubility modeling (Mrs. R. Berner, E. O. Glasser, et. al.) of cement containment of nuclear waste, and with a report of a preliminary evaluation of near field radioactivity release from neutron activated reactor parts buried in a shallow site at Oak Ridge, Tennessee. B. G. J. Thompson, et. al., reported on independent efforts of the United Kingdom's Dept. of the Environment to evaluate proposals from the nuclear industry for the burial of nuclear waste and outlined their program.

#### Poster Sessions L5 through 12

Poster sessions were held in the evening. These sessions provided a good opportunity to meet the authors and to discuss the work. Papers from the poster sessions will be included in the published proceedings of the meeting and cover essentially the same general areas as the oral sessions.

#### Session L5 - Waste Form Performance: Spent Fuel

W. J. Gray presented a poster addressing the topic of the a 100 times greater uranium release from spent fuel than from unused UO<sub>2</sub>. This reason for this increase was not established and work is continuing but some of the increase was attributed to oxidation of the UO<sub>2</sub> and effects of combined alpha, beta and gamma radiation. N. H. Uziemblo, et. al. reported on characterization of solids from hydrothermal tests with spent fuel in a rocking autoclave and found low concentrations of radionuclides after six months. Most reaction products were from the nonradioactive nuclear waste. This work would need to be carried out for a longer time and specific reactions identified. Detection of actinides in groundwater using laser acoustic spectroscopy was reported by Mark M. Duxtader, et. al. Van Konynenburg, et. al. reported on a continuation

of their earlier work on carbon-14 release in a tuff repository. The earlier paper was available at the poster and showed analyses of the rapidly released carbon and indicated that more data are needed on the slower release of carbon and on the life time of the canister to determine if gaseous release of C-14 meets the regulation requirements.

#### Session L6 - Metal Corrosion

A poster by Sharland discussed several techniques of modeling long-term pit propagation in waste canisters. The complexity of the problem has lead to the necessity for a number of physical and chemical approximations in the modeling. The applicability and ranges of validity of several of the more common approximations investigated, and the predictions with experimental pit growth rates were compared. An investigation of the sensitivity of the models to the various empirical input parameters indicates which parameters need to be determined most accurately. Finally, a steady-state model of cavity propagation and a more sophisticated numerical model which involves a finite element technique and yields both steady-state and time-dependent solutions was discussed.

Another model for predicting corrosion of nuclear waste containers was presented by J. C. Walton and coworkers. This mechanistic model for corrosion of high-level waste containers in an aqueous environment is being formulated by the Basalt Waste Isolation Project. Electrochemical charge-transfer reaction kinetics are used in conjunction with transport of reactants and products due to Fickian diffusion, hydrodynamic dispersion and fluid advection. The model provides for a choice of oxidants from among water, oxygen, sulfate, and radiolysis products. The model user may elect to study effects of any combination of these oxidants.

Anatamula and Fish did a poster on work performed and reported earlier when Umtanum basalt flow was the reference repository horizons; the current BWIP reference horizon is the Cohasset flow. While their data is now outdated, they did indicate plans for work on cast steel A216, Cu90-Ni10, and PDO Copper (high phosphorus deoxidized Cu).

J. H. Haberman reported on corrosion behavior of mild steel under simulated salt repository conditions and found that corrosion in solid salt was less than corrosion in brine, corrosion was affected by heat treatment and microstructure of the steel and increases in magnesium in the environment increased the corrosion rate of the steel.

#### Session L7 - Low-Level Waste and Materials

#### Session L8 - Materials Interactions

G. B. Mellinger of the Materials Characterization Center presented a poster on the standardized test methods to demonstrate compliance with acceptance specifications. Standardized test methods expected from the MCC include radionuclide release tests, recommended practices for chemical, radiochemical and microstructural analyses, method for determining waste form expansion, internal canister corrosion test and others. Some tests available from the American Society for Testing and Materials will be used.

#### Session L9 - Waste Form Performance: Glass

#### Session L10 - Radiation Effects

The poster by Greigor, et. al. represented a cooperative effort of Boeing Aircraft, Univ. of New Mexico and the General Electric Co. to study a pyrochlore of the type  $A_{1-2}B_2O_6Y_{0-1}$ . This structure could serve as host for various radioactive species substituting in the A, B and C sites. S. Nicolosi presented a poster concerned with the development of a mechanism for the radiolysis of bicarbonate containing groundwater.

#### Session L11 - Groundwater Chemistry and Interactions

#### Session L12 - Rock/Backfill Performance

There were two posters from Finland in this session, M. Snellman, et. al. and A. Muurinen and P. Penttila-Hiltunen, one from Sweden, Roland Pusch, one from France, H. Coulton, et. al. and one from the U. S., E. L. Russell, et. al. The Finland investigators studied the effect of bentonite in radionuclide speciation and solubility in the near field of a granite repository. They found that bentonite will affect the chemical conditions in a repository and suggested that a realistic description of the effect of parameters such as water composition, clay/water ratio, degree of compaction and temperature should be studied. The French paper reported on swelling clays, smectites, and on nonswelling clay, illite. Russell, et. al. reported on a model for a nuclear waste repository embedded in salt.

#### Session L13 - Materials Interactions

This session had papers dealing with degradation and leaching of nuclear waste glass (R. B. Heimann, F. J. Ryerson, et al. and R. Bazan, et al.) and effects of steel and iron corrosion products on the nuclear waste glass performance. G. Bart, et al. and B. Grambow, et al. discussed the effects of steel corrosion products on the leaching process. There appears to be some evidence that the rate of leaching is increased in the presence of steel corrosion products. One of the papers was by T. E. Jones, et. al. and described development of a tracer injection system for characterizing reactions of waste materials under hydrothermal conditions.

#### Session L14 - Waste Performance: Glass

The papers in this session dealt with waste glass leaching. Chemistry and kinetics of waste glass leaching and most aspects of modeling of glass were discussed by B. C. Bunker who stated that his approach was objective in terms of his not working with nuclear waste disposal. He talked about complex glass compositions, complex solution chemistry and leached layer effects. He discussed network hydrolysis, interdiffusion or chemically controlled diffusion, chemical diffusion in terms of hydrolysis, water diffusion, and free energy of hydration, solution chemistry models and dissolution rate vs. saturation. He concluded that the greatest uncertainties in leach predictions are due to our lack of understanding of the surface layer and that an understanding of network hydrolysis is needed. Papers specifically dealing with leaching mechanisms included those by X. Feng and A. Barkatt, T. A. Abrajano, et al., R. D. Aines, et al., and F. Lanza, et al. Some of the results presented at the meeting were from reports recently reviewed under the NBS/NRC program. There was more emphasis on mechanisms of the leaching process, with which investigators are becoming more familiar, than was evident in previous reports. The mechanism involves diffusion of an ionic acid species (possibly  $H_3O^+$ ) into the glass and the simultaneous outward diffusion of alkali ions. Network forming species (for example Si, B or oxide ions containing these elements such as  $HSiO_4$ -tend to be removed at a much slower rate. This process leads to the formation of a gel covering the glass which consists of remaining network forming materials. Most aspects of the modeling of the glass leaching process were summarized. Progress in modeling efforts and the significant problems concerning the chemistry and kinetics of waste glass leaching were outlined. Also of interest were papers by D. F. Bickford and D. J. Pellarin describing results of large scale leach studies.

#### Session L15 - Radiation Effects

The papers dealt with radiation effects on copper corrosion (W. H. Yunker and R. S. Glass, W. H. Smyrl, et. al.), oxidation of actinides in salt solutions (J. I. Kim, et. al.), effects of radiation on groundwater chemistry and the waste package (W. L. Ebert, et. al. and M. A. Lewis and D. Reed). Smyrl, et al.'s found that kinetics of Cu corrosion in low concentrations of  $H_2O_2$  are identical to kinetics for dissolved oxygen. At higher concentrations of  $H_2O_2$ , this similarity disappears and Cu oxidizes to  $Cu^+$  (not  $Cu^{++}$ ) producing a  $CuCl$  film on the surface. In the paper by Yunker on NNWSI experience on long term corrosion in  $\gamma$  radiation environment, liquid and gas phase exposures at 95 and 150 C with air present, it was concluded that corrosion with irradiation is about an order of magnitude greater than that without irradiation. In private communications with Anatumula, this author indicated that in air/steam the BWIP program formed a one order-of-magnitude increase in corrosion rate due to radiation; and the corrosion behavior at 150 C was like that at 250 C.

#### Session L16 - Groundwater Chemistry and Interactions

M. I. Wood, et al. and C. A. Cederberg, et al. focussed on the adsorption process as species migrated into surrounding packing material. Some of the important leachate species such as Pu and Tc have a tendency to undergo reduction and be adsorbed or precipitate from the groundwater. There appears to be good evidence that reduced actinide species have a strong affinity for basalt or bentonite so that a large fraction of will be immobilized, or the rate of migration will be impeded.

#### Session I5 - Defect Characterization

Bentley and Miller, ORNL, Metals and Ceramics Division, had an interesting poster in Session I5 on Waste Form Performance. The poster dealt with combined atom probe and electron microscopy characterization methods for fine-scale structures in aged primary piping of stainless steel. Size limit for detection was given as of the order of 5 Angstroms. Their methods seem suitable for detection of the precursor to precipitates that cause sensitization of stainless steels. We plan to look at their work further to determine whether their methods will be useful in our assessments of potential sensitization problems in stainless steels proposed for use in repository environments.