Evaluation and Compilation of DOE Waste Package Test Data

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ABSTRACT

This report summarizes evaluations by the National Institute of Standards and Technology (NIST) of Department of Energy (DOE) activities on waste packages designed for containment of radioactive high-level nuclear waste (HLW) for the six month period August 1988 through January 1989. Included are reviews of related materials research and plans, activities for the DOE Materials Characterization Center, information on the Yucca Mountain Project, and other information regarding supporting research and special assistance. NIST Comments are given on the Yucca Mountain Consultation Draft Site Characterization Plan (CDSCP) and on the Waste Compliance Plan for the West Valley Demonstration Project (WVDP) High-Level Waste (HLW) Form.

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EXECUTIVE SUMMARY

This is the sixth biannual progress report by the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), that deals with assessments of the Department of Energy (DOE) activities related to the waste package for disposal of radioactive high-level waste (HLW). This report contains NIST reviews conducted over the period August 1988 to January 1989 on DOE reports related to activities of the Nevada Nuclear Waste Storage Investigation (NNWSI). In 1989, the NNWSI program name was changed to the Yucca Mountain Project (YMP), and hereafter will be called the (YMP). Status reports given here highlight the NIST assessments of DOE activities relating to nuclear waste storage at Yucca Mountain, NV. In addition, a summary is given for the activities of the DOE-sponsored Materials Characterization Center (MCC).

Ten reviews of technical reports on various pertinent topics are included in this report. Two of these deal with container materials. One report deals with the effects of gamma radiation on the engineered barrier system and addresses the effects of radiation on the corrosion behavior of steel and copper. Their results indicate that the oxidizing nature of the environment is increased, but not enough to cause pitting of the stainless steels or copper and its alloys. In the other report, the effects of hydrogen peroxide (an expected production of radiation) on corrosion of copper are examined, with the conclusion is that the mechanism of corrosion in this environment would be the same as that in the oxygen found in the repository environment.

There are five reviews on the waste form. Three are on glass and in one of them it is concluded that dissolution of glass is more rapid in pure water than in repository water. Another, on modeling, describes the factors that must be considered in developing a model that can predict long-term effects. The third report on the glass waste form leaching behavior is modeled. In this report, a theoretical study on the durability of glass, the author is able to show a direct correlation between glass durability and its free energy of hydration calculated from the composition of the glass.

Two reports are on the topic of spent fuel. One report states plans (but no new data) for determining fuel dissolution and the rate of release of radionuclides from failed fuel. The other report on spent fuel is a study of variations in radionuclide release from cladding with and without defects, using four types of specimens.

A report on water chemistry develops a geochemical model (EQ 3/6) that permits considerations of long-term interaction effects between the water and the minerals of a repository. A number of unanswered questions are presented in the review of this 1979 report.

A report on the first generation of conceptual models for performance of a nuclear waste package is reviewed. Models for various processes that affect a waste package are given, e.g., thermal, corrosion, transport. Interactions among heat source, heat transfer, fluid flow, mechanical stress, and general corrosion are supported in this computer code.

The process of developing a design for containment of nuclear waste is described. The factors of corrosion resistance, mechanical properties, weldability, and cost, are considered in the choice of suitable materials. Through a ranking system developed for this study, five metals are chosen, and these are: AISI 304L, 321, 316 stainless steels, Incoloy 825, and 1020 carbon steel.

Appendix D includes some technical comments on the draft of the NNWSI Site Characterization Plan. Other comments had been submitted previously. These comments deal mostly with the waste package container, and there are a few comments on the environment, the waste form and peer review.

A more detailed report on the Material Characterization Center's (MCC) activities is included in Appendix E. Some data are given on the round robin Product Consistency Test (PCT), and indications are that some improvements in the test and a more complete description of the statistical analysis are needed. In other glass work involving the MCC-3 pulsed flow tests for leach rate, the ATM-10 and CUA (UVCM-10) glasses were more durable than the CTS (SF-6) glass. The results were similar to those obtained using the static leach test, MCC-1.

Acknowledgements

The editor wishes to thank the following contributors to the production of this report:

The following contributing reviewers authored the reviews and evaluations given in Appendix B -- Dr. T. Ahn, Dr. U. Bertocci, Mr. E. Escalante, Dr. A. Fraker, Dr. H. Ondik, Dr. E. Plante, and Dr. J. Wasylyk.

Ms. Joyce F. Harris who typed this report and coordinated production of the reviews included in this report.

Mr. Steven Harrison and Ms. Carla Messina who have continued to develop applications software for the NIST/NRC Database for Reviews and Evaluations on High-Level Waste (HLW) Data.

The authors acknowledge the various reviewers of this report for their helpful suggestions. The Project Manager, Mr. Charles H. Peterson and his colleagues at the NRC, Mr. Lewis Ives, the NIST WERB reader and Mr. David B. Anderson, the Metallurgy Division Reader.

1.0 INTRODUCTION

1.1 Background

This is the sixth biannual progress report to the Nuclear Regulatory Commission (NRC) from the National Institute for Standards and Technology (NIST). These reports deal with the NIST assessments of the Department of Energy (DOE) activities related to the waste package for disposal of radioactive high-level waste (HLW). The NIST provides the NRC with critical reviews and evaluations of research, reports and publications and has established a database for the reviews. The NIST also provides the NRC with data from laboratory measurements designed to verify or establish failure mechanisms of materials being considered for use in nuclear waste storage.

The Yucca Mountain Project (YMP) deals with the storage site at Yucca Mountain, Nevada. This site was selected in December 1987 as the primary site in the United States for the first nuclear waste repository. This report covers NIST activities under FIN A4171 for the period from August 1988 through January 1989. Material and activities reported deal only with NNWSI reports or other material pertinent to disposal of high-level waste at Yucca Mountain.

1.2 Reviews and Evaluations

The reviews and evaluations conducted by the NIST over the period August 1988 to January 1989 are included as Appendix B. Contributing reviewers for these reviews are acknowledged as a group on the cover page of this report. Reviews are created using guidelines that are modified periodically. The guidelines describe for reviewers the types of information to be contained in each section of a review. The current version of the guidelines for reviewers is presented as Appendix A (pp. A-1 to A-6). The reviews are presented as Appendix B (pp. B-4 to B-66), and brief summaries are given in Section 3.0.

The DOE is actively engaged in programs for the vitrification of high-level radioactive waste in borosilicate glass. Both the West Valley Demonstration Project (WVDP) at West Valley, NY, and the Defense Waste Processing Facility (DWPF) located at the Savannah River Plant in Savannah, GA, will soon be producing vitrified high-level waste (HLW). NIST activities in this area during this reporting period included the reviews on the glass waste form (Appendix B) and our evaluation of the document entitled "Waste Compliance Plan for the West Valley Demonstration Project High Level Waste Form", WVDP-055 West Valley, New York, 1986. This 1986 waste

compliance plan was revised in late 1987. Comments on the 1986 plan are given in Appendix C. Chapters of PNL-5157 are being reviewed at the present time. Independent reviews on each of the seven chapters of that report are being written by the NIST. These chapters were written by experts in the field and contain much valuable information that needed critical evaluation. It is planned to combine the reviews of all these chapters of PNL-5157. The document, PNL-5157, contains much useful information but it must be stated that since that time, the MCC, WVDP, DWPF and other laboratories have conducted much glass-leaching research on compositions as related to leaching and use in nuclear waste storage. Also, test method development has advanced for standardizing glass leaching tests.

Activities of the DOE-sponsored Materials Characterization Center (MCC) and the status of selected MCC test methods are discussed in Section 2.2. Details are presented in Appendix E. The MCC monthly reports over the past two years show considerable progress on test development work for glass leaching, production of approved testing materials and determination of effects of impact from dropping waste canisters.

1.3 Database Activities

The NIST/NRC Database for Reviews and Evaluations on High-Level Waste uses a new database management system (DBMS), Advanced Revelation®, and the conversion has been completed. Conversion of the NIST/NRC files from the previously used DBMS, Revelation®, into Advanced Revelation® was completed in the previous reporting period, and experience using the "Advanced" version has been highly satisfactory.

During this reporting period, two data elements were added in efforts to broaden search and listing capabilities for the database. The database had been structured in a manner that permitted searching on or listing of any of the authors, but sometimes lists or searches of the principal author(s) are required. The database was modified to permit listing of or searching on the principal author. This was done by creation of a new data element. Likewise, a data element was created so that sort and search operations can now be performed on the publication date.

In addition, software was written to permit the porting of any of our Revelation® files into a format suitable for use by the Center for Nuclear Waste Regulatory Analyses (CNWRA). Using this program, called DATAOUT, the bibliographic file, which is contained in the WORK.REF

file, was transferred to a 5-1/4 inch, 1.2 Mb floppy disk and mailed to the Center. About 1000 references were included in that transmittal.

1.4 Related Laboratory Testing

Studies involving laboratory testing at the NIST are continuing in four areas. Since the results of these studies will be reported separately at appropriate stages of the work, no reports on these studies are included in this report. The objective of these laboratory tests is to confirm the accuracy of DOE data and the validity of the conclusions deduced from it. Topics of these four studies are as follows: (1) Evaluation of Methods for Detection of Stress Corrosion Crack Propagation in Fracture Mechanics Samples, (2) Effect of Resistivity and Transport on Corrosion of Waste Package Materials, (3) Pitting Corrosion of Steel Used for Nuclear Waste Storage, and (4) Corrosion Behavior of Zircaloy Nuclear Fuel Cladding. One of the tasks under, study 4, was a review of corrosion of Zircaloy. This review was released to the NRC in March 1988. Results from studies 2 and 3 were presented at the symposium on Corrosion of Nuclear Waste Containers at the 174th Meeting of the Electrochemical Society, October 9-14, 1988. Additional results from the other laboratory testing will be also published upon completion of selected parts of these works.

2.0 DOE Activities

The location and environment at Yucca Mountain are discussed briefly in this section. Other topics covered are DOE activities, waste package materials, vitrification activities and the Materials Characterization Center (MCC).

2.1 Yucca Mountain -- Location and Environment

The Yucca Mountain site has been described in previous reports, but the information is included again for the convenience of the reader and to establish the environment which must be considered for waste package durability. Briefly, the NNWSI site is located in Nye County in southern Nevada and is in the Topopah Spring Member of the Paintbrush Tuff at Yucca Mountain. The tuff material is a devitrified volcanic rock and contains approximately 12 percent porosity and five volume percent water [Soo et al. 1985; McCright et al. 1983]. The waste package environment during the containment period probably will be gamma irradiated (10^4 rd/h for spent fuel and 10^3 rd/h for glass waste) moist air and tuff rock.

The atmosphere at the Yucca Mountain storage site is oxic. Initial temperatures resulting from the nuclear waste storage will depend on design and a number of factors but the peak temperature could range around 300°C and taper off to about 100°C after 300 y. Temperatures will remain at this level for many more years. The pressure is expected to be one atmosphere.

The repository will be located above the water table, and moisture will be present. At the present time, water flow is limited, and has been estimated to be six to eight millimeters per year, but this could change. The waste packages will be above the boiling point of water for many years and water vapor will be present. When the cooling period begins, small amounts of water will be present due to condensation and infiltration. Other sources of water would be ground water from various sources and water which could be formed as a result of other reactions. Conditions of wetting and drying will exist, and the concentration of salts will result from this wetting and drying process.

The pH of the water is expected to be buffered, with naturally occurring sodium bicarbonate, to a near neutral pH of 7.1, or it could become slightly alkaline. However, it must be considered that the pH could shift to the acidic range. Radiolysis of N_2 , O_2 , H_2O mixtures could cause the pH to shift into the acidic range. Another potential source of pH change is alternate wetting and drying.

2.1.1 Yucca Mountain Site Characterization Plan

The development of a Site Characterization Plan for the Yucca Mountain repository is a step that points the way toward consolidation of direction and effort for the site. The NIST provides technical and scientific interpretation of the many documents being produced by the DOE. The NIST emphasis is on corrosion related issues, but reviews are included that impact on the corrosion of the waste package canister. The NIST reviewed the Consultation Draft Site Characterization Plan (CDSCP) for Yucca Mountain, and developed sixteen critical comments for consideration by the DOE. These were submitted to the NRC, and are given in Appendix D.

During the past six month period, seven reviews have been completed on the subjects of (1) container materials alloys, (2) waste glass, (3) spent fuel, (4) water chemistry, and (5) waste package performance modeling. A brief description of these reviews is found beginning in 3.1.1.

Issues related to licensing involved in these reports have been identified previously, and these issues are as follow:

- a. The effect of gamma radiation on corrosion.
- b. The rate of leaching of waste glass.
- c. The potential release of radionuclides from spent fuel based on the durability of the cladding.

2.2 Materials Characterization Center

The Materials Characterization Center (MCC) was organized by the Department of Energy (DOE) in 1980 to ensure that qualified data on nuclear waste materials would be available. The MCC is located in the state of Washington and operated by the Pacific Northwest Laboratories (PNL) of the Battelle Memorial Research Institute. About sixty percent of the MCC funding comes directly from the DOE, with the balance coming from other DOE offices. The MCC issues monthly reports in addition to specific project reports. The original MCC objective were as follow:

- a. Develop standard test methods.
- b. Test nuclear waste materials using these methods.
- c. Publish these test procedures and data in a Nuclear Waste Materials Handbook.
- d. Develop approved test materials (ATM) and approved reference (ARM) materials and provide these to others as needed.

Since October, 1988, the MCC monthly reports state that the objective is to support waste management programs, and objectives given in the monthly reports are as follow:

- a. Provide well characterized test materials and test material documentation.
- b. Conduct testing of waste package components in support of waste form qualification.
- c. Provide assistance related to enhancing the quality and interlaboratory consistency of analytical data obtained by these programs.
- d. Conduct independent tests to confirm data obtained by others related to the behavior of waste package components.

The MCC monthly reports for July through December, 1988 have been reviewed for the present document, and sections listed by the MCC follow. The sections on Support to the Salt Repository Project and the Basalt Waste Isolation Project were discontinued after September 30, 1988. The MCC work in each of these sections is summarized in Appendix E.

- A. Program Administration
- B. Quality Assurance
- C. Support to the Office of Facilities Siting and Development
- D. Support to the Salt Repository Project
- E. Support to the Basalt Waste Isolation Project
- F. Support to the Defense HLW Technology Program
- G. Support to the Savannah River Laboratory
- H. Support to the West Valley Demonstration Project

3.0 NIST Activities

3.1 Reviews and Summaries

Technical reviews completed during the reporting period are presented in Appendix B. All reviews presented there have been approved by the NIST Washington Editorial Review Board (WERB). A brief summary of these reviews follows.

3.1.1 Container Materials

Glass, Van Konynenburg, and Overturf: 1985

In the engineered barrier system, the effect of gamma irradiation in the air-steam environment expected in the repository continues to be a matter of primary concern. This report considers the effects of irradiation on the corrosion processes at the metal surface for stainless steels and copper-based alloys. Specifically, the study considers the production of oxidizing species, such as hydrogen peroxide and hydroxide radicals, and their effect on the corrosion process. The results indicate that the oxidizing nature of the environment is increased, but not enough to cause pitting of the stainless steels or copper and its alloys.

Smyrl, Bell, Atanososki, and Glass: 1986

The effect of hydrogen peroxide, expected to form in irradiated water, on the corrosion of copper is examined in this study. The authors show that the oxidation of copper increases as the concentration of hydrogen peroxide is increased. This effect is almost indistinguishable from the effects of oxygen, and the authors conclude that the corrosion mechanism for either the same.

3.1.2 Waste Form

3.1.2.1 Glass

Mendel: 1984

This report evaluates the effect of the environment on the rate of glass leaching. Both laboratory and field tests indicate that the leaching rate of most elements from glass is less in groundwater than in pure water, and this is attributed to the high concentration of silicon already present in groundwater, with the presence of silicon in high concentrations leading to a decrease in the driving force for glass dissolution. However, colloid formation with iron in the water and sorption of glass species by bentonite tend to increase the rate of glass dissolution, and as concentrations of dissolved species reach saturation levels, the dissolution rate decreases. The authors indicate that longer term testing is required before many of the questions regarding glass dissolution can be answered.

Mendel: 1984

Some computer modeling of waste glass leaching has been developed for short time periods (<1 y), but none have been developed for the long-term exposures (hundreds or thousands of years) anticipated in a repository post-closure period. This report describes the factors that must be considered in developing a model that can predict long-term effects, and describes the development of a model that considers the initial kinetic-controlled reactions and the transition to steady-state behavior that will exist for the long term.

Jantzen: 1988

In this report, a theoretical study on the durability of glass, the author is able to show a direct correlation between glass durability and its free energy of hydration calculated from the composition of the glass. This relationship is supported by results from an earlier laboratory study on leach rates of 155 different glasses.

3.1.2.2 Spent Fuel

Shaw: 1987

The rate of release of radionuclides from failed waste-form containers is of primary consideration in this plan for studies. This plan coupled with the referenced SCP, addresses many of the questions that need to be considered in any determination of radionuclide release from spent

fuel. This report describes test plans and provides no new data. The plans include determinations of the following: dissolution rates and rates of release for spent fuel, chemistry of water in contact with spent fuel, oxidation of UO_2 , corrosion testing of cladding, and modeling of these processes.

Wilson and Shaw: 1986

This study examines the dissolution of spent fuel from defective and defect-free cladding. Four types of specimens are used: the first is completely intact cladding without defects, second is cladding with two 0.01-inch-diameter laser-drilled holes, third is cladding with a slit (1-inch long by 0.006-inch wide), and finally fuel pellets without any cladding. As expected, the release rate from the bare fuel was higher than for any of the other cladding configurations. Oxidation of the stainless steel reduced the concentration levels of the radionuclides in solution by reacting and precipitating out of solution, and increasing the temperature of the environment did not consistently change the dissolution behavior of the spent fuel.

3.1.3 Water Chemistry

Wolery: 1979

Development of an understanding of long-term interactions between the local geological formations and groundwater at repository conditions is of utmost importance. This study uses two models, EQ3 and EQ6, to develop a more sophisticated model, EQ3/6, which allows long-term interaction effects to be considered. Results are compared with other existing and well known geochemical codes.

3.1.4 Waste-Package Performance Modeling

O'Connell and Drach: 1986

This report describes the development of an integrated assessment of the performance of the nuclear waste container that uses existing computer codes. The rationale, assumptions, and framework for using these codes is discussed. The model considers effects of radioactive decay, groundwater, corrosion, alteration of waste form, and radionuclide release. This is a first generation model that will be used to develop later models. Localized corrosion, such as pitting and stress corrosion are not considered at this stage of development.

3.1.5 Container Design

Russell: 1983

The process of developing a design for containment of nuclear waste is described. The factors of corrosion resistance, mechanical properties, weldability, and cost, are considered in the choice of suitable materials. Through a ranking system developed for this study, five metals are chosen, and these are: AISI 304L, 321, 316 stainless steels, Incoloy alloy 825, and 1020 carbon steel.

Appendix A. Guidelines for Reviewers of Reports on
Waste-Package Data

Appendix A

Guidelines for Reviewers of Reports on Waste-Package Data

DATA SOURCE

Full document reference. This section may be completed for the reviewer before he/she receives the document. If completing this section yourself, use the following format:

TECHNICAL REPORT:

Pitman, S. G., "Slow-Strain-Rate Testing of Steel,"
Rockwell Hanford Operations, SD-BWI-TS-008, August 1984.

CONFERENCE PAPER:

Abrajano, T. A., Jr. and Bates, J. L., "Transport and Reaction Kinetics at the Glass: Solution Interface Region: Results of Repository-Oriented Leaching Experiments," in Materials Research Society, 1983 Symposia Proceedings, Vol. 26, Scientific Basis for Nuclear Waste Management, McVay, G. L. (editor), North-Holland, 1984, p. 533-542.

DATE REVIEWED

Give the date the document review was completed. Add an additional date each time that the review is revised, e.g. 11/25/86; Revised 12/01/86.

PURPOSE

If the author states the purpose, give that; if not, give your perception of what the purpose must have been.

KEY WORDS

These are to be checked off on the key word checklist. In general, these keywords should reflect the information given in the above categories discussed above. Additional keywords, which are truly different from terms on this list, should be added to the list under the category "other" which appears at the end of each key word list.

CONTENTS

List the number of pages, figures and tables, and some breakdown (as appropriate) of subsections, e.g. literature survey 15 p, test methods 2 p, discussion 1 p.

TYPE OF DATA

- (1) Scope of the Report, e.g. Experimental, Theoretical, Literature Review, Data Analysis.
- (2) Failure Mode or Phenomenon Studied, e.g. Corrosion, Creep, Fatigue, Leaching, Pitting, Hydrogen Embrittlement, Debonding, Dealloying

MATERIALS/COMPONENTS

Description of the material studied, e.g., 304L stainless steel, brass, zircaloy cladding, welds in 316 stainless steel, packing material, basalt. Also describe, if specifically addressed, component parts, e.g. the screw-type cap on a waste cylinder.

TEST CONDITIONS

- (1) State of the material being tested -- cold worked or annealed 304L stainless steel, thermo-mechanical history of the material (or component) studied.
- (2) Specimen Preparation -- prestressed, precracked, size, type of specimen.
- (3) Environment, pressures, and other test parameters of the material being tested, e.g. aqueous environment, radioactive surrounding, electrolytes or corrosive agents present, temperature and pressure (externally applied or not) during the test.

METHODS OF DATA COLLECTION/ANALYSIS

This section includes data measurement methods and types of data measured, as well as data analysis techniques, e.g. electron microscopy, weight loss vs time, slow strain rate, tensile test, x-ray diffraction, differential thermal analysis, A.C. electrical resistivity using a Wheatstone bridge, mass spectroscopic chemical analysis of the corrosive environment, Latin Hypercube method, Monte Carlo techniques.

AMOUNT OF DATA

This section includes the number of tables and graphs together with their titles and axes (including the range in values). If a listing of figure and table titles is

provided, the reviewer should add the limits given on each axis, i.e. for temperature, or other explanatory information as appropriate.

Sometimes a synthesis is preferable to a listing of table and figure titles:

Five tables of temperature and time data for five molten-glass pouring operations, each table including the data from ten sensor locations. The temperatures ranged from 1100°C to 0°C over a time period of 24 hours.

UNCERTAINTIES IN DATA

Included here are error bars and uncertainties in the data as stated by the author. This also includes qualitative statements by the author on the reliability of the data:

The author states that, "Temperatures carry an accuracy of +5°C while the times are reported to within +15 sec. It was felt that under real glass pouring operations (without well controlled crucible cooling) the temperature-time curves will be shifted to somewhat higher temperatures than shown here."

DEFICIENCIES/LIMITATIONS IN DATABASE

Statements by the author on the applicability of the data are given here:

The author states "Extrapolation of the temperature-time (time < 24 hrs) data presented here to times in excess of 100 years should not be performed." The data presented here is useful only for indicating trends and qualitative parameter relationships, not for the purpose of presenting absolute values.

CONCLUSIONS

Put the conclusions of the author in quotes whenever the author's words are used without interpretation or paraphrasing.

COMMENTS OF REVIEWER

The reviewer's general comments on the document. This category is wide open as far as content. It contains information the reviewer did not enter into any of the above categories, but which is considered important for the reader to know. It is also in this section that the reviewer would put any of his/her comments on the deficiencies and uncertainties in the data and analysis:

This is a very comprehensive review of the literature on the temperature sensitization of stainless steels. Even though it neglects the definitive work of Bertocci, Shull, Kaufman, and Escalante [Phys. Rev. J13, (1979), pp. 15-358] in this area (presumably because of the difficulty in locating this document), this review still considers a sufficiently large number of other investigations to provide a good understanding of the present status of the field. The one discordant note here, however, is that it would have been a much more useful review if stainless steel types 301, 303, 304, 316, and 440°C had also been addressed.

Statements such as, "Further tests in this area are needed," or "More data is required," require an explanation. To state the need is valuable; such statements, however, do not provide enough information.

Abstracts taken from the document to be reviewed will be attached to the review. The abstract is also available in the database. Therefore, references to the abstract may be made.

RELATED HLW REPORTS

The report number(s) of any report(s) known to be directly related to the report being reviewed should be entered here so that these reports may be cross-referenced in the database.

The reviewer might also indicate any other reports taken from the reference list (in the report being reviewed) that should be acquired and included in the database.

APPLICABILITY OF DATA TO LICENSING -- READ, BUT DO NOT COMPLETE THIS SECTION, NOT TO BE FILLED IN BY THE REVIEWER

Indicated here is the licensing issue addressed by this paper. It is either (a) a specific Listed licensing Issue in an NRC Site Characterization Plan (ISTP) or (b) a new issue not yet identified in an ISTP.

The ranking of the paper is determined as follows: The "Key Data" box is marked if the paper contains data that is deemed to be of sufficient quality that it must be considered by NRC in an evaluation of a license application. Such a paper must meet at least one of the following criteria: (1) it is an in-depth review of the pertinent literature, (2) it contains data that is found to be especially significant after being assessed for scientific merit and quality, or (3) it contains data with

such a small uncertainty that it must be considered in a performance evaluation of a license application. If the paper does not meet any of the above three criteria, it is indicated as "Supporting Data".

Reviewer's comments on the listing of the document may be included with the appropriate Issue Listing in subcategory (a) or (b).

AUTHOR'S ABSTRACT

The author's abstract is given whenever available. Usually, it presents key numerical data. Whenever it does not, the reviewer is asked to furnish key numerical data within the review. These key data may be placed in any appropriate section of the review.

Appendix B. NIST Reviews of Documents Concerning the
Durability of Proposed Packages for High-Level
Radioactive Waste

Appendix B

NIST Document Reviews Concerning the Durability of Proposed Packages for High-Level Radioactive Waste

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Shaw, H. J., UCID-21272 Plan for Spent Fuel Waste Form Testing for NNWSI	B-34
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Water Chemistry

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Waste Package Performance Modeling

O'Connell, W. J. and Drach, R. S., UCRL-53761

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Russell, E. W., McCright, R. D., and

O'Neal, W. C., UCRL-53449

"Containment Barrier Metals for High-Level
Waste Packages in a Tuff Repository" B-65

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Lawrence Livermore National Laboratory for the U.S.
Department of Energy
Contract No. W-7405-Eng-48.

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

Glass, R. S., Van Konynenburg, R. A., and Overturf, G. E.
"Corrosion Processes of Austenitic Stainless Steels and
Copper-Base Materials in Gamma-Irradiated Aqueous
Environments."
UCRL-92941, September 1985.

DATE REVIEWED: 11/29/88; Revised 12/12/88; 12/20/88.

PURPOSE

This paper presents old data (from UCRL-92311) on the electrochemical behavior of austenitic stainless steel in the presence of γ -irradiation and H_2O_2 , together with similar data concerning pure copper (CDA-102).

KEY WORDS

Experimental data, scoping test, electrochemical, laboratory, J-13 water, gamma radiation field, ambient pressure, ambient temperature, copper base, stainless steel, 316L stainless steel, CDA102 copper, open circuit potential, corrosion (irradiation).

CONTENTS

Text: 7 pages, 6 figures, of which only 3 are new. 2 Tables, both old.

AMOUNT OF DATA

Apart from repeating data on stainless steel, the paper contains:

Fig. 4. Open circuit potential vs. time for Cu/J-13 water: effect of switching γ -irradiation on and off.

Fig. 5. Open circuit potential vs. time for Cu/J-13 water: effect of adding one drop of 30% H_2O_2 .

Fig. 6. Photograph of CDA 102 rod after irradiation at 3 Mrd/h for 15 days, half immersed in J-13 water, half in contact with moist air.

TEST CONDITIONS

J-13 water + γ -irradiation (3.3 Mrd/h), or + addition of a drop of 30% hydrogen peroxide. $T = 30^{\circ}\text{C}$.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

"Gamma irradiation increases the oxidizing nature of the aqueous solutions used in this study through production of $\bullet\text{OH}$ and H_2O_2 . These species probably account for the observed positive corrosion potential shifts for stainless steels, copper, and copper alloys. The observed corrosion potentials are mixed potentials, resulting from a complex superposition of all the cathodic processes (e.g., reduction of $\bullet\text{OH}$, O_2 , and H_2O_2) and anodic processes (e.g., metal dissolution) occurring at the metal surface."

"Copper and its alloys are known to be very catalytic towards the decomposition of H_2O_2 , a radiolytic product. In solution, the surfaces of copper and its alloys appear to be more affected (oxidized) in irradiated environments than those of stainless steels. With regard to corrosion potential shifts under irradiation, the same general behavior as for stainless steels (positive corrosion potential shifts) is observed initially. However, the corrosion potentials then decline to relatively less positive values. This may be related to a decreased efficiency for catalytic decomposition of H_2O_2 , resulting from surface oxidation or adsorption of intermediate species."

"In addition to the work reported above, preliminary results from other experiments involving stainless steels, copper, and copper alloys in J-13 well water and its concentrated forms (to 100x), show that the positive corrosion potential shifts observed under irradiation are not sufficient to shift the metal into the pitting corrosion regime. Detailed studies are currently underway to evaluate the effect of irradiation on localized corrosion susceptibility (e.g., to pitting and crevice corrosion) of prospective nuclear waste container materials."

COMMENTS OF REVIEWER

There is no section called "Conclusions". The part reported in the preceding section is called "Summary". Therefore, it is not surprising that the first two paragraphs are essentially a restatement of the results, which look quite reasonable. They show that for Cu, they are qualitatively in agreement with the belief that the principal effect of γ -irradiation is to provide a local, oxidizing environment, dominated by the presence of hydrogen peroxide. However, these data do not yet lead to an estimation of the corrosion rate in the repository, nor do they give any information on the likelihood of localized attack.

In the last paragraph, the authors mention that "preliminary results" indicate that γ -irradiation does not seem to increase the danger of pitting. However, no data are presented. If these encouraging results are nothing more than the two curves in Fig. 11 of UCRL-92311, this reviewer does not think that there is anything to be encouraged about.

RELATED HLW REPORTS

1. Glass, R. S., Overturf, G. E., Van Konynenburg, R. A., and McCright, R. A., "Gamma Radiation Effects on Corrosion: I Electrochemical Mechanisms for the Aqueous Corrosion Processes of Austenitic Stainless Steels, UCRL-92311 (1985).
2. Reed, D. T., "Effect of Ionizing Radiation on Moist Air Systems," UCRL-97936 (1987).

APPLICABILITY OF DATA TO LICENSING

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

- (a) Relationship to Waste Package Performance Issues Already Identified

2.2.4.2 Effects of radiation on the corrosion failure modes and associated corrosion rates for the waste package container

- (b) New Licensing Issues

- (c) General Comments

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Lawrence Livermore National Laboratory for the U.S.
Department of Energy
Contract No. W-7405-Eng-48.

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

Smyrl, W. H., Bell, B. T., Atanososki, R. T., and Glass,
R. S.
"Copper Corrosion in Irradiated Environments. The
Influence of H_2O_2 on the Electrochemistry of Copper
Dissolution in HCl Electrolyte."
UCRL-95961, December 1986.

DATE REVIEWED: 1/25/89.

PURPOSE

To study the effect of hydrogen peroxide on the anodic
dissolution of copper in hydrochloric acid.

KEY WORDS

Experimental data, general corrosion, electrochemical,
laboratory, Cl, acidic solution (ph <7), ambient temperature,
copper base, Cu, corrosion (general).

CONTENTS

12 pages, 7 figures, 13 references.

Cyclic voltammograms and polarization curves for Cu in 0.1 M
HCl with and without hydrogen peroxide.

TEST CONDITIONS

Deaerated solutions at 25°C.

UNCERTAINTIES IN DATA

According to the authors the experimental results are
reproducible.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

At low hydrogen peroxide concentrations the relationships between current, electrode potential and transport conditions in solution are identical to those found in the presence of oxygen, which indicates that the mechanism is the same, namely, that the corrosion rate is under transport control. Deviations observed at hydrogen peroxide concentrations higher than 0.01 M, can be due, according to the authors, either to direct reaction of hydrogen peroxide with the metal, or to an indirect mechanism which enhances the formation of a cuprous chloride film.

COMMENTS OF REVIEWER

The experimental work is O.K., but there is little more than already known in the literature. The tentative explanation given to the results obtained at high hydrogen peroxide concentrations is open to some doubt. A more reasonable interpretation would probably entail consideration of chloride transport toward the electrode also, since the deviations from the behavior predicted from the data at low hydrogen peroxide concentrations are observed at the higher current densities.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.2.8 How will the design of the waste package container accommodate all potential natural and waste package induced conditions?

(b) New Licensing Issues

(c) General Comments

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Pacific Northwest Laboratory operated for the Department of Energy by Battelle Memorial Institute, Columbus, OH.
Contract No. DE-AC06-76RLO 1830

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

Clark, D. E. and Hench, L. L.

Mendel, J. E., Compiler

"Final Report of the Defense High-Level Waste Leaching Mechanisms Program; Chapter 3, Environmental Interactions."

PNL-5157, August 1984.

DATE REVIEWED: 8/17/87; Revised 9/20/88; 4/7/89.

KEY WORDS

Literature review, leaching, corrosion, weight change, pH measurement, laboratory, air, carbon dioxide, N₂, basalt composition, deionized, groundwater, tuff composition, silicate water, acidic solution (pH <7), ambient pressure, dynamic (flow rate given), high temperature, static (no flow), glass (defense waste reference glass), PNL 76-68, TDS-131, ABS-39, ABS-41, SRL-165, matrix dissolution (glass).

CONTENTS

43 pages with 12 figures, 13 tables, 41 references.

AMOUNT OF DATA

Tables

Table 3.1--"Groundwater Chemistries for Several Geologies (Analysis, ppm)." The analysis is listed for 13 ionic species, as well as the pH and the Eh (volts), for basalt, granite, and salt locations. Data are given under the basalt heading for Grande Ronde, Interbed, and Upper Wanapum locations; under the granite heading for Stripa Mine and Nevada Test Site locations; and under the salt heading for WIPP Brine Inclusions and WIPP Dissolved Core.

Table 3.2--"Reference Materials Used in This Investigation." Data are given [units not given, probably ppm] for nine ionic constituents and the pH for Reference Synthetic Groundwater, Stripa Groundwater, MCC Reference Silicate Water, and MCC Reference Brine.

Table 3.3--"Effects of atmosphere on DWRG Leaching. Test conditions were 90°C, 28 days, SA/V = 0.1 cm⁻¹ and deionized water." The pH, normalized total mass loss (g/m²) and relative standard deviation (%) are given for ambient atmosphere, pure CO₂, and pure N₂.

Table 3.4--"Effects of Ground Water on DWRG Leaching Under Dynamic Testing Conditions; Monolithic Samples, 90°C." The table lists the pH and the leachate concentration (mg/L) for nine elements for pure synthetic groundwater, for groundwater and deionized water after leaching, for time periods of 4 or 28 days, for SA/V ratios (m⁻¹) of 10.7, 10.5, 266, and 224.

Table 3.5--"Normalized Total Mass Loss (based on weighing) for DWRG Under Several Environmental Conditions." Mass loss data (g/m²) are given for 12 leachants, three flow conditions, and for periods of 1, 3, 6, and 12 months.

Table 3.6--"Effects of Ductile Iron on DWRG Leach Rates in Dynamic Tests with Ground Water; Monolithic Samples, 90°C." The pH and the leachate concentration (mg/L) are given for nine elements for four and 28 days of testing.

Table 3.7--"Effects of Solution Chemistry on Release of Pu-239, Np-237, and U from doped DWRG, 56 days, 90°C, Static, SA/V = 0.1 cm⁻¹. Amounts of the three elements are given in ppb for three test solutions, each with and without Fe.

Table 3.8--"Summary of Leach Solution Data from Uranium-Doped DWRG." Data are given for B, Fe, Na, Si, and Sr in ppm for 14-, 28-, and 56-day test periods in DI water and in DI water with Fe. All tests were at 90°C with SA/V = 10 m⁻¹.

Table 3.9--"Summary of Leach Solution Data from Plutonium-Doped DWRG." Data are given for B, Fe, Na, Si, and Sr in ppm for 14-, 28-, and 56-day test periods in DI water and in DI water with Fe. All tests were at 90°C with SA/V = 10 m⁻¹.

Table 3.10--"Summary of Leach Solution Data from Neptunium-Doped DWRG." Data are given for B, Fe, Na, Si, and Sr in ppm for 14-, 28-, and 56-day test periods in DI water and in DI water with Fe. All tests were at 90°C with SA/V = 10 m⁻¹.

Table 3.11--"Summary of Leach Solution Data from Plutonium-Doped DWRG (SGD-Pu)." Data are given for Al, B, Ca, Fe, Na, Si, and Sr in ppm for 14-, 28-, and 56-day test periods in basalt groundwater and in basalt groundwater with Fe. All tests were at 90°C with SA/V = 10 m⁻¹.

Table 3.12--"Summary of Leach Solution Data from Neptunium-Doped DWRG (SDG-Np)." Data are given for Al, B, Ca, Fe, Na, Si, and Sr in ppm for 14-, 28-, and 56-day test periods in basalt groundwater and in basalt groundwater with Fe. All tests were at 90°C with $SA/V = 10 \text{ m}^{-1}$.

Table 3.13--"Average %RSD Between Leachate Samples." Values are given for pH and Na, Li, Si, and B for seven leachants for various time periods of the tests reviewed in this report.

Figures

Figure 3.1--"Boron and Lithium Concentrations and Normalized Total Mass Loss Due to Leaching DWRG in Deionized Water, synthetic Silicate Water and STripa Water Under Static Conditions." The B concentration in ppm (from 0 to 4.0), the Li concentration in ppm (from 0 to 2.0), and the normalized total mass loss in g/m^2 (from 0 to 4.0) are plotted versus the corrosion time in days (from 0 to 28).

Figure 3.2--"FTIRRS Analysis Before and After Leaching for 28 Days at 90°C in (a) Stripa Groundwater with $SA/V = 0.1 \text{ cm}^{-1}$, (b) Stripa Groundwater with $SA/V = 1.0 \text{ cm}^{-1}$, and (c) Deionized Water with $SA/V = 0.1 \text{ cm}^{-1}$. Hatched areas correspond to the range of values obtained with several samples." Reflectance in percent (from 0 to 40) is plotted versus wavenumbers (from 1400 to 400).

Figure 3.3--"Schematic Illustrating the Relationship Between Concentration, Contact Time, Flow Rate and Leach Rate." Three diagrams show the relationship between concentration and contact time, between concentration and flow rate, and between leach rate and flow rate.

Figure 3.4a--"Boron Concentrations Resulting from Leaching DWRG in Deionized Water and Silicate Water Under Flowing Conditions." Three diagrams show boron concentration (ppm) versus corrosion time for tests at 90°C, and $SA/V = 0.1 \text{ cm}^{-1}$. For static testing, cell volume 30 mL, the boron concentration from 0 to 4.0 is plotted versus time from 0 to 28 days. For 0.1 mL/h flow testing, cell volume 60 mL, the boron concentration (0 to 2.0) is plotted versus time from 0 to 9 months. For 1.0 mL/h flow testing, cell volume 60 mL, the boron concentration (0 to 1.0) is plotted versus time from 0 to 28 days.

Figure 3.4b--"Lithium Concentrations Resulting from Leaching DWRG in Deionized Water and Silicate Water Under Flowing Conditions." Three diagrams show lithium concentration (ppm) versus corrosion time for tests at 90°C, and $SA/V = 0.1 \text{ cm}^{-1}$.

For static testing, cell volume 30 mL, the lithium concentration from 0 to 2.0 is plotted versus time from 0 to 28 days. For 0.1 mL/h flow testing, cell volume 60 mL, the lithium concentration (0 to 4.0) is plotted versus time from 0 to 9 months. For 1.0 mL/h flow testing, cell volume 60 mL, the lithium concentration (0 to 1.0) is plotted versus time from 0 to 28 days.

Figure 3.4c--"Strontium Concentrations Resulting from Leaching DWRG in Deionized Water and Silicate Water at a Flow Rate of 0.1 mL/h." The diagram shows strontium concentration (ppb) from 0 to 80 versus corrosion time (days) from 0 to 112 for tests at 90°C, and SA/V = 0.1 cm⁻¹.

Figure 3.4d--"pH Versus Time for the Deionized Water and Silicate Water Exposed to DWRG." Three diagrams show pH versus corrosion time for tests at 90°C, and SA/V = 0.1 cm⁻¹. For static testing, cell volume 30 mL, the pH from 5 to 10 is plotted versus time from 0 to 28 days. For 0.1 mL/h flow testing, cell volume 60 mL, the pH from 6 to 10 is plotted versus time from 0 to 6 months. For 1.0 mL/h flow testing, cell volume 60 mL, the pH from 4 to 10 is plotted versus time from 0 to 28 days.

Figure 3.4d--"Normalized Total Mass Loss (g/cm²) Versus Time for DI Water and Silicate Water With and Without Iron, and Stripa Water Exposed to DWRG." The diagram shows normalized total mass loss from 0 to 40 versus corrosion time from 0 to 42 days for static testing at 90°C, and SA/V = 0.1 cm⁻¹, and cell volume 30 mL.

Figure 3.5--"Illustration of Two Effects on Leaching Characteristics of PNL 76-68 Glass, i.e., Effect of Groundwater Without Iron Present and Effect of Having Iron Present During Leaching." For boron and cesium, the normalized g•m from 0 to 45 is plotted versus time in days from 0 to 32 for tests at 90°C, SA/V = 10 m, in tuff, basalt, and DI water environments.

Figure 3.6--"Elemental Concentrations, pH and Normalized Mass Loss Versus Corrosion Time for DWRG in Deionized Water Containing Iron Coupons or Powders." Data are for 28-day static tests, SA/V = 0.1 cm⁻¹, at 90°C, without iron, with iron coupons, and with iron powders. Silicon concentration (ppm) is plotted from 0 to 25, boron concentration (ppm) is plotted from 0 to 5, pH is plotted from 5 to 10, and normalized total mass loss (g/cm²) is plotted from 0 to 12.

Figure 3.7--"SEM-EDS of DWRG Corroded in Deionized Water Containing Iron Coupons or Powders." Two micrographs are shown with diagrams on which relative intensity is plotted against energy. No scales are given. The test conditions are those of static testing, 14 days, 90°C, SA/V = 0.1 cm⁻¹.

Figure 3.8--"Comparison of DWRG Leaching Behavior in Deionized Water and Deionized Water Plus Iron at a Flow Rate of 1.0 mL/h, Temperature Equal to 90°C and SA/V = 0.1 cm⁻¹. (a) pH versus time, (b) Boron concentration versus time, (c) Sodium concentration versus time, (d) Lithium concentration versus time, (e) Silicon concentration versus time, (f) Magnesium concentration versus time, (g) Iron concentration versus time, (h) Aluminum and strontium concentration versus time, (i) Normalized total mass loss." All data are plotted versus the corrosion time from 0 to 28 days. In (a) the pH scale is from 4.0 to 10.0. In (b) the boron concentration scale is from 0 to 12 ppm. In (c) the sodium concentration scale is from 0 to 30 ppm. In (d) the lithium concentration scale is from 0 to 12 ppm. In (e) the silicon concentration scale is from 0 to 65 ppm. In (f) the magnesium concentration scale is from 0 to 40 ppb. In (g) the iron concentration scale is from 0 to 14 ppm. In (h) the scale for aluminum and strontium concentration is from 0 to 16 ppm. In (i) the normalized total mass loss (g/m²) scale is from -60 to 30.

Figure 3.9--"Comparison of DWRG Leaching Behavior in Deionized Water, Silicate Water and Silicate Water Plus Iron at a Flow Rate of 0.1 mL/h, Temperature Equal to 90°C and SA/V = 0.1 cm⁻¹. (a) pH versus time, (b) Boron concentration versus time, (c) Strontium concentration versus time, (d) Normalized total mass loss versus time." In (a) and (d) the time scale is from 0 to 12 months. In (b) and (c) the time scale is from 0 to 112 days. In (a) the pH scale is from 6.0 to 10.0. In (b) the boron concentration scale is from 0 to 2.5 ppm. In (c) the strontium concentration scale is from 0 to 80 ppb. In (d) the normalized total mass loss is from 0 to 70 g/m².

Figure 3.10--"Total Alteration Thickness (microns) Versus Leach Time for DWRG Under a Variety of Environmental Conditions. Thickness corresponds to the depth of alteration excluding pits." Total gel thickness (μm) from 0 to 3 is plotted versus corrosion time (months) from 0 to 6. Data for seven environments are shown, all at 90°C and SA/V = 0.1 cm⁻¹.

Figure 3.11--"SIMS Analysis of Buried Samples and One Laboratory Sample of Nuclear Waste Glasses. The depth of leaching corresponds to the depth from which boron was removed from the glass. All samples were exposed to 90°C." Samples

were buried at the Stripa Mine, and in granite and in bentonite environments. Relative counts are plotted from 0 to 10 on an arbitrary log scale versus depletion depth from 0 to 16 in μm .

Figure 3.12--"Boron Depletion Depth Versus Time for Several Nuclear Waste Glasses Exposed to Various System Components. All data was obtained from samples exposed to 90°C." Penetration or depletion depth from 0.1 to 100 μm on a log scale is plotted versus time from 10 to 1000 days on a log scale.

TEST CONDITIONS

(1) State of the Material being Tested

Glass monoliths
DWRG (^{239}Pu -doped)
DWRG (^{237}Np -doped)
DWRG (U-doped)

(2) Specimen Preparation

Information not given.

(3) Environment of the Material being Tested

Solutions used:

Air-Saturated Deionized Water, pH = 5.68.
Nitrogen-Saturated Deionized Water, pH = 7.0.
Jones Reference Synthetic Silicate Water, pH = 9.75.
Simulated Hanford Site Basalt Ground Water.
Tuff Ground Water from Well J-13 at the Nevada Test Site.
Stripa Ground Water, pH = 9.1 and 8.3.
MCC Reference Silicate Water, pH = 7.5.
MCC Reference Brine, pH = 6.5.

Temperature: 90°C.

Contact (flush) time: 60 h, 28 days, 600 h, 1 month, 56 days, 3 months, 6 months, 12 months.

Leachant flow rates (mL/h): 0.1, 1.0.

Surface area exposed to solution volume ratio (SA/V) (cm^{-1}):
0.1, 1.0, 4.0, 10.0, 10.3, 10.5, 10.7, 224, 266.

Secondary (overpack) components: ductile iron, rock, stainless steel, bentonite.

Atmospheres: ambient (oxic), pure CO_2 , pure N_2 .

Field conditions, granite boreholes.

Leachant pH: 5.68, 7.0, 7.0 to 7.2, 7.5, 9.0.

Leachant Eh (zeta potential, mV), > -80, -37, -25 to -40, -10.

UNCERTAINTIES IN DATA

Exact repository conditions for DWRG immobilized nuclear waste are not yet known with certainty. Data presented in this report were studied for variables bounded by conditions as now perceived to be present in a repository at storage start up.

Statistical basis for data are discussed in Section 3.8 - Appendix. All data in this review represent averages of at least two determinations. Error bars are indicated on most of the figures listed in the chapter.

DEFICIENCIES/LIMITATIONS IN DATABASE

Longer term data are needed to verify the reliability of performance predictions.

COMMENTS OF REVIEWER

Laboratory and field system measurements were carried out to evaluate the effect of these variables on the leaching mechanisms. In comparison to pure or deionized water, the rates of leaching of most elements are decreased in ground water and increased in the presence of bentonite and ductile iron (under oxic conditions). Ground water contains relatively large concentrations of silicon which reduces the amount of silicon that can be extracted from the glass before saturation is reached and thus decreases the driving force for glass dissolution. Iron causes the formation of colloids while bentonite provides sorption sites. Both of these effects reduce the effective concentration of glass species thereby increasing the extraction from the glasses.

Field tests conducted several hundred meters underground at the Stripa mine in Sweden indicated that the relative leach behaviour of various waste glasses were the same as displayed in laboratory experiments. High SA/V ratios in the burial tests, which more closely approximate the physical conditions in the repository, also lead to low waste glass leaching rates due to the same saturation effects observed in laboratory tests.

Of course, since low leach rates are identified with saturation, it follows that flow will increase leach rates. The sorption effects of bentonite which increase the leach rate of glass appear to diminish in time which may be associated with saturation of sorption sites. In this report no effects on leaching behavior were observed with stainless steel but it has since been observed that leach rates may be increased by stainless steel which has been sensitized by weldments.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.5 how will packing, container materials (including overpacks, canisters, and any special corrosion-resistant alloys or spent fuel rod cladding, if applicable) and/or their alteration products interact with the waste form to cause its alteration and/or effect release of radionuclides?

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Pacific Northwest Laboratory operated for the Department of Energy by Battelle Memorial Institute, Columbus, OH. Contract No. DE-AC06-76RLO 1830

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

Barkatt, A., Macedo, P. B., and Montrose, C. J.

Mendel, J. E., Compiler

"Final Report of the Defense High-Level Waste Leaching Mechanisms Program, Chapter 6, Phenomenological Models of Nuclear Waste Glass Leaching."

PNL-5157, August 1984. Available from NTIS.

DATA REVIEWED: 7/20/88; Revised 10/31/88; 11/5/88.

PURPOSE

Chapter 6 of this report reviews and discusses mathematical models describing the mechanisms of nuclear-waste glass leaching under a wide range of environmental conditions. The models will serve the purpose of providing long-term predictions of nuclear-waste-glass leaching.

KEY WORDS

Literature review, model, leaching, altered glass-surface, gel-layer and precipitate-layer, interactive leach-model, diffusion, matrix dissolution, ion migration, electric double layer, hydration energy, thermodynamic equilibrium, crystalline silicates, mineral dissolution, rock weathering, adsorption and description, phenomenological model, Quartz, Muscovite, K-Feldspar, Diopside, Forsterite, Nepheline, SRL-131, DI water, dispersion, leachant renewal time, Peclet number, flow, Pyrex, Obsidian, CUA, NBS borosilicate, window glass, CAS, SRL-165C, M3, M5, M7, IDAHO-1277, LLNL-529, PNL 76-68, Frit, ESF.

CONTENTS

Chapter 6 of this report consists of 16 pages which include an executive summary, a background, 1 table, 8 figures, 27 equations, and the following number of pages covering each topic listed:

<u>Topic</u>	<u>Pages</u>
Kinetics of Aqueous Attack	2.0
Interactive Modeling Approaches	1.5
Thermodynamic Models	1.5
Reaction Kinetic Models	2.0
Mathematical Phenomenology of Glass	
Leaching: a Non-Mechanistic Model	4.0
Diffusion - Controlled Dispersion of Leach	
Products	2.0
References	2.0

AMOUNT OF DATA

The calculated data with experimental verification are included in 4 figures and 2 places in the content. The dimensions of the presented data are:

$\log_{10} [kg/0 \cdot t]$ (-4 to 4) versus leach rate slope (0 to 1.2)
where K is the high-dilution rate constant for silica dissolution,

D is the silicon species diffusion coefficient in the protective layer of thickness ℓ , and
q is the proportionality constant in the relationship between the amount of silica leached and ℓ .

Free Energy of Hydration, Kcal/mol (3 to -18) versus
Normalized Si Loss, g/m^2 (0.4 to 10^3)

Total Immersion Time, day (10 to 10^3) versus Leachant
Concentration, mg/L (10 to 10^3).

Leachant Renewal Time, $day \cdot m^{-1}$ (10 to 10^5) versus Normalized
Concentration mg/L (1 to 10^4).

Immersion Time, day (10 to 10^3) versus concentration, mg/L
(10^2 to 10^3).

TEST CONDITIONS

In most cases, one-dimensional analysis was performed using a leaching source (glasses) of a fixed concentration in (1) infinitely diluted leachants, (2) leachants with varying concentration, and (3) saturated leachants. Occasionally, the glass surface had layers of protection, gel and precipitates. In rare cases, two-dimensional analysis was performed using cylindrical coordinates in intact or fractured glasses with infinitely diluted leachants.

The following summarizes assumptions, the state of waste forms, environmental conditions, and main leaching-mechanisms.

(1) classical approach

- The diffusion of mobile ions through the glass network.
- Matrix dissolution and surface layer mass transfer.

(2) A protective layer formation

The processes described in (1) classical approach quickly reach their equilibrium, after which protective layers form on the glass surface. These are the porous alteration (gel) and the protective precipitation-layers. At a steady state, silicon-containing species are diffused through the protective layer, balancing the rate of silicon dissolution.

(3) Interactive modeling approach

Leaching is highly sensitive to leachant concentrations which can vary up to the solubility limit at low or even moderate flow rates. The solubility limit can be predicted by thermodynamics.

(4) Thermodynamic approach

Since the contact-time of leachant with glasses is very long in repository, the leachant is expected to be saturated with respect to surface precipitates, arriving at a thermodynamic equilibrium state.

(5) Reaction kinetic approach

The kinetics of mineral dissolution are used in waste glasses because the precipitate-layer on the glasses is crystalline and both have similar base-structure of silicates. Glass dissolution is rate-controlled by surface reaction because of low solubility. Precipitation rates can be added, as the rates of backward-reaction, to the overall reaction rates.

(6) A non-mechanistic approach

A semi-empirical description is presented both with one's intuition and conclusions regarding the importance of specific processes. One example of such processes is the concentration overshoot of leachants. The leachant concentration is the time-integral of accumulation rates of dissolved species. In interactive cases, the accumulation rates can be any function of the integral itself.

(7) Dispersion of leach-product approach

The dissolved species are dispersed by diffusion and convection from intact or cracked glasses to stagnant or low flow-rate groundwater.

UNCERTAINTIES IN DATA

The stated uncertainties in adjustable parameters or subsequently calculated results using these parameters are:

(5) Reaction kinetic approach: The silicon dissolution rates are proportional to n th power of proton activity. The exponent n varies from -0.2 to 0.6 in basic solutions.

(7) Dispersion of leach-product approach: the backfill porosity is 10~20%.

Many parameters have uncertainty ranges, though not stated by the authors. Such parameters include diffusivities of mobile species in solid and liquid, reaction-rate constants, the thickness of altered layer, supersaturation parameter, and waste form dimension.

DEFICIENCIES/LIMITATIONS IN DATABASE

The authors state following deficiencies/limitations in models. More comprehensive evaluation by the reviewer is given in the section entitled GENERAL COMMENTS.

(1) Classical Approach

Diffusion-controlled kinetics are inadequate to account for the observed leaching data. The modification with moving boundary conditions still do not represent the fundamental physical and chemical processes. The formulation is only credible under conditions of an extremely diluted leachant.

(2) A protective layer formation

A carefully constructed treatment of the interplay of protective-film formation and solubility-controlled dissolution must be incorporated into a realistic model of leaching process.

(3) Interactive modeling approach

- Michiels and Pescatore: The effects of temperature and pH need to be described independently, and alteration layer and precipitation should be considered.
- Michiels and Sullivan: The evolution of surface layer has not been integrated with an approach that accounts for changes in solution chemistry.
- Grambow: The rates of formation or the distribution of precipitates within the layer have not been considered.

(4) Thermodynamic approach

- The choice of structural units in calculating free energies of hydration is arbitrary.
- Species interactions, such as the formation of alumino-silicates, are ignored.
- The application of equilibrium thermodynamic considerations to a fundamentally dynamic situation is only justifiable post-hoc.
- The use of MCC-1 tests without some definite stages of interaction may invalidate the model.

(5) Reaction kinetic approach

After the initial fast dissolution of preferentially attacked glasses, the rates slow down to those of bulk materials, but the overall rates curve of linear kinetics was misinterpreted by parabolic kinetics.

(6) A non-mechanistic approach

The non-linear response functions were approximated to be an elementary product form. Each element of the product uses empirical exponential-decay-form without justifications.

Quantitative prescription is lacking for evaluating the long-time limiting concentration of various elements.

(7) Dispersion of leach product approach

The diffusivity of mobile species in the contacting leachant is too slow, leading to a very short leachant-renewal-time.

CONCLUSION OF AUTHOR

There is not a conclusion section in this report. The following is from the Executive Summary and several discussions in content.

1. The continued leaching of waste glass under almost any given set of conditions ultimately leads to steady-state (or quasi steady-state) concentrations of all leached species.
2. The models developed depend largely on dissolution-rate-constants, effective diffusion coefficients, saturation concentration and identity of alteration products.

3. No comprehensive model is available for the prediction of leaching in geological times. It may be a zero-exponent time-law in saturated conditions, deduced from 1/2 and 1 exponent time-laws in short-term kinetics.
4. The saturated condition in geological times can be predicted through the calculation of the thermodynamic equilibrium state.
5. The observed concentration-overshoot can also be predicted by a semi-empirical approach, which includes the expansion of accumulation rates with respect to the total concentration.
6. The diffusion and convection are equally important in the long-term dispersion of radionuclides from glasses to surrounding environments.

COMMENTS OF REVIEWER

The classification and evaluation of leaching models made by authors are very good, showing the distinctive scientific-merits of representative models: classical leaching-kinetics, the role of protective layer(s), the effect of leachant concentrations, the thermodynamic prediction, the non-mechanistic approach, and the dispersion model. However, some areas need to be reorganized or complemented for better understanding.

The relevant data in generic glasses need to be addressed. Phase separation is an example which was not considered seriously in waste glasses. When the phase-separated microstructures are interconnected, they are likely to be preferentially attacked along easily susceptible phases. Other localized attacks are pits observed in ancient glasses and the spallation of precipitates or gel layers. The authors need to address how these phenomena are viewed or explained with respect to existing models.

The report should be more comprehensive regarding the extent to which each article was evaluated, particularly, in its assumptions, applicabilities or limitations. The concentration overshoot or the decrease of dissolved-ion concentration in long-term have been modeled in at least three different ways: solubility limit by Apted, supersaturation by Harvey, and semi-empirical correlation by Macedo group. Certainly all of them fit the experimental data well. Therefore, it is desirable to understand each model by developing a more comprehensive evaluation to find out reasons for such a coincidence.

The author did not address the time-dependence of glass surface area which may be significant as the amount of precipitates are increased. Also, the growth kinetics of precipitates layer need attention. Any modifications in the growth kinetics may alter leaching kinetics significantly. Many works in solid state chemistry provide mechanistic kinetics rather than a linear correlation to total leachant concentration. Such an example is the diffusion-controlled kinetics of oxide scale growth. Also the possibility of homogeneous precipitates should be considered in leach models. Incorporation of surface precipitates in leach rates are briefly considered in crystalline silicates by authors and in the model developed by Wallace and Wicks. More extensive evaluation is necessary, including homogeneous precipitates in solution. Classical theory and works by Harvey or McCoy and Markworth do not include surface or bulk precipitates. The authors need to find out how these models are justified without them.

The solution effects may need to be evaluated more specifically, though mentioned briefly as a controversy using thermodynamics in dynamic equilibrium. When solubility limit is used in multicomponent glasses, the solubility limit for one component will affect the dissolution rates of others which are not yet at saturated conditions. Therefore, verifying the model with short-term tests in unaltered solutions may not be valid.

Also, the solution pH is a time-varying function caused by either the hydrolysis process or by the occluded cell formation in severely cracked glasses. This concept was not considered in any models quoted.

The role of flow rates was analyzed quantitatively by Hughes group. It shows several regimes of flow-rates where diffusion-rates, flow-rates, or leach-rates are dominant. Perhaps it would be worth while for the authors to point out whether conditions made by Hughes group can limit the use of each model described in the content. Furthermore, other relevant models for flow-rates effects were not included. An example of this type of work was developed by McCoy and Markworth.

The authors should have informed us that it was unclear as to whether the glass surface was in contact with the saturated leachant or not. Pigford group assumed that the leachant was saturated on the glass surface while other groups (Wicks, Harvey and Lasaga) did not. Are the kinetic effects responsible for the unsaturated leachant on the glass surface?

For instance, during precipitations, the leachant concentration near precipitates or in leachant solution are not necessarily saturated in diffusion-limited kinetics for geological times. The unsaturated region can extend to a longer distance in leachants.

The author may need to address the justification of leach-rate equations in interactive cases. There is no reason why the leach-rates are first-order kinetics, and should not be formulated as second-order kinetics which are closer to the experimental values observed by Harvey.

Works on the geometric effect of waste form or leaching paths have been neither considered nor mentioned, except for one-dimensional analysis; Such examples are formulations in the performance of the whole waste package known to us by the codes WAPPA and PANDORA (even though they are very primitive codes).

Radiation decay or radiolysis is largely missing. These radiation effects may lead to the modification of existing models or to the development of completely new one. To obtain this knowledge, the author needs to evaluate the codes WAPPA and PANDORA.

The real scenario of waste glass leaching needs to be addressed. An example of this is the modification of the Pigford model, considering glass wetting through a pin-hole in a container. Also, the authors should extend their evaluations to the up-to-date and modified Pigford model by McVay group, incorporating temperature, pH and Eh.

The introduction part in 6.6 non-mechanistic model is lengthy because it reiterates previous formulations and underlying mechanisms made by others. Perhaps the statement beginning with (6.13) along with a detailed discussion of figure 6.6 is sufficient to explain this model.

In the calculated results, very little attention was given to uncertainty analysis caused by doubt associated with physical parameters.

More specific comments not evaluated by authors are as follow for each classification of models:

6.2 Kinetics of aqueous attack

- The picture of gel-layer and the precipitates-layer are opposite to that made by Aagaard.
- In obtaining the exponent of time-law, caution should be given: such a plot is only valid asymptotically when viewed over a long time period.

- It has not been confirmed that leach rates are decreased with the increased surface area at low leachant concentrations

6.3 Interactive model

In the model made by Harvey, leach rates can be zero, according to the authors' evaluation. There is no justification for the existence of supersaturation.

6.4 Thermodynamic models

Following the normalization of leachant concentration with silicon concentration, we should also normalize the axis of solution pH). It is well known that leachant concentration versus solution pH has a minimum value of leachant concentration approximately at pH=7, in short-term testing rate-controlled by diffusion or matrix dissolution. Therefore, both the kinetic model and the thermodynamic model predict the same results. The authors should explain this coincidence.

6.5 Reaction Kinetic Model

In working forward or backward reactions, it may not be possible to have a precipitate reaction if the leachant concentration is far from equilibrium on which the dissolution kinetics were formulated.

6.6 Non-mechanistic Model

In long-term extrapolation of phenomenological equations, the probability of obtaining misleading results due to uncertain parameters is greater than that which exists in the mechanistic model. This is because the uncertainties associated with the mechanistic model can be estimated, while those associated with non-mechanistic model can not.

6.7 Diffusion-controlled dispersion

In Hughes model, leach rates should be time-dependent, which will alter the calculated domains significantly. The model is valid in a very large amount of leachant. Are the extreme values derived from the model at increased flow rates consistent to other models?

RELATED HLW REPORT

This report is a comprehensive summary of existing literature in leaching model. Therefore, all reports or papers quoted should be included in data base, separately.

APPLICABILITY OR DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to NNWSI ISTEP issues.

- 6.2 Classical leaching model
- 6.2 Role of protective layer in leaching
- 6.3 Role of solution concentration in leaching
- 6.4 Thermodynamic model of leaching in confined and stagnant solutions
- 6.7 Dispersion of leach products

(b) New Licensing Issues

- 6.5 Leaching kinetics of crystalline silicates as complementary tools for glass leaching
- 6.6 Application of non-mechanistic model

(c) General Comments on Licensing

The Chapter 6 of this report summarizes and evaluates a number of pertinent leach models which need to be better formulated prior to licensing waste package.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

E.I. du Pont de Nemours & Co., Savannah River Laboratory
Contract No. DE-AC09-76SR00001

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

Jantzen, C. M.
"Prediction of Glass Durability as a Function of Glass
Composition and Test Conditions: Thermodynamics and
Kinetics."
DP-MS-87-157, June 1988.

DATE REVIEWED: 1/12/89.

PURPOSE

"The relative role of kinetics and thermodynamics in predicting the long-term durability of glasses will be examined" by theoretical modeling and experiments.

KEY WORDS

Theory, experimental data, (thermodynamics, precipitation reaction), leaching, solubility, inductively coupled plasma (ICP) atomic adsorption (AA), laboratory, ASTM TYPE I high-purity water, basic (alkaline) solution (pH>7), neutral solution (pH=7), static (no flow), 55 nuclear waste glasses (West Valley Defense, and unspecified) and 100 natural and man-made glasses including 4 ancient glasses, monolith, crushed to various mesh sizes, hydration, matrix dissolution.

CONTENTS

This report consists of 17 pages which include abstract, an introduction, 7 figures, 12 equations, and the following number of pages covering each topic listed:

<u>Topic</u>	<u>Pages</u>
Theoretical:	
Glass Durability: A Function of Glass Composition	1.5
Glass Durability: A Function of Glass Structure	1.0
Glass Durability: A Function of Test Parameters	2.5
Experimental Results:	1.0
Glass Durability: A Function of Glass Composition	1.5
Glass Durability: A Function of the Kinetic (SA/V)t	

<u>Topic</u>	<u>Pages</u>
Parameters	1.0
Discussion and Conclusions	1.0
References	1.5
Figures	4.0

AMOUNT OF DATA

There are seven figures. Four figures are normalized mass losses with three figures showing ranging from 0.1~10000g/m² versus free energy of hydration -20 to 10 Kcal/mole and a fourth figure showing the normalized mass on a scale of .01 to 1000 g/m² versus -20 to 10 Kcal/mole. Another figure shows Silicon release of 0.1 to 10000 ppm versus surface area/solution-volume x time (0 ~ 400 days/cm). The final two figures are three dimensional: free energy of hydration (-13.49 ~ 4.96) versus surface area/solution x time (70 ~ 163082) versus log (silicon release) (-0.82 ~ 3.44).

TEST CONDITIONS

Modeling

- Isotropic assumption was used for thermodynamic approach.
- One-dimensional analysis was adopted while varying the ratio of glass surface to solution volume, for glass leaching and precipitation.
- Glasses have various compositions, structures, and surface layers. They can be monolith or crushed glasses.
- The thermodynamic approach requires the thermodynamic equilibrium between glasses and aqueous environments, but does not require determination of the time dependent kinetics of leaching processes.
- Concentrations are assumed to be proportional to the ideal ion activities in the thermodynamic treatment. The overall free energy of hydration of glass is a summation of fractional functions of that of individual silicate and oxide components.
- The free energies of hydration of glasses are correlated with both the ionic potential and the ionic field strength, and glass structure is not considered to be an additional parameter affecting glass durability.
- The kinetic approach has nth (unspecified) order dissolution rates for forward reaction and for precipitates reaction as backward reaction. Both rates are proportional to nth power of proton activity.
- The precipitation rates can be expressed with an equilibrium constant, concomitantly and with free energy change associated with the precipitation.

Experiment

ASTM Type I high-purity water was used at 90°C. Four 4cm² surface area of glass monoliths and 1.5g of crushed glasses to various mesh sizes were immersed in 40 cm³ solutions. The test duration was 28 days.

UNCERTAINTIES IN DATA

Modeling

The quoted error bars in thermodynamic approach are as follows: "95% upper and lower confidence limits determined for the combinations of free energy of hydration, log (normalized Silicon release), log (normalized Boron release), and pH. The primary contribution to the 95% was from free energy of hydration and errors in glass analysis are more significant than errors in leachate analyses." There was no specification of error associated with kinetic parameters such as rate constants of dissolution and precipitation, and the free change associated with precipitation.

Experimental

"All glass compositions are summed to 100 and have errors of 100 + ±5 wt%." The detailed analyses of errors in experiments are not given.

DEFICIENCIES/LIMITATIONS IN DATABASE

Modeling

"Since the hydration thermodynamic approaches assume that glass structure is a primary function of glass composition, glass structure is not considered as an additional parameter affecting glass durability."

Experimental

"The solutions were not filtered and the fines were not removed from the crushed glass by an alcohol wash. This is thought to contribute to some of the observed variability in the data." Concentrations were assumed to be proportional to ideal activities in thermodynamic treatment. (Underlines are made by reviewer)

CONCLUSION OF AUTHOR

There are sections entitled (1) Discussion and Conclusions, and (2) Abstract. Conclusions drawn from the contents of these sections are as follows:

The durability of a glass is a function of its thermodynamic and kinetic stability in solution. Glass durability has been shown to be a function of thermodynamic free energy of hydration which can be calculated from the glass composition. Hydration thermodynamics also furnish a quantitative frame of reference to understand how the various test parameters affect the glass durability.

Different test conditions result in different kinetic parameters and this would be true for the following variables: the exposed glass surface area, the leachant solution volume, and the length of leaching time. The relative durabilities of glasses define a plane in three-dimensional -- free energy of hydration, concentration, glass surface area·time·solution volume -- space. At constant kinetic conditions, the three-dimensional plane is intersected at a constant value of the parameter glass-surface-area·time/solution-volume and the plotting of the free energy of hydration versus concentration has a similar slope.

The combined kinetic and thermodynamic contributions to glass durability have been verified experimentally by defining a plane in the above dimensional space at constant temperatures. The experimental data was obtained from nuclear waste, commercial, and ancient glasses.

COMMENTS OF REVIEWER

This report contains much useful information in both modeling and experimental work on glass durability. The most impressive merits are: (1) an excellent correlation between glass durability and free energy of hydration despite a large disparity of materials in which Si losses differ by a factor greater than 300, (2) numerous data for 155 glasses including nuclear waste, ancient, and man-made glasses; and, (3) a new kinetic model incorporating a precipitation reaction as a backward reaction. However, some areas should be clarified and need to be studied further.

The correlation of the material's loss with free energy of hydration is an approach of reversible thermodynamics, while kinetic description is an approach of irreversible thermodynamics. The former is a static situation while the latter is a dynamic situation. It is very unclear how these two approaches are adopted in interpreting experimental data. Did the proposed equilibrium arrive at 90°C after 28 days? Are the quoted data obtained by Newton and Paul at 25°C for 24 hours comparable to the present data? Further, material's loss was found to be dependent on the ratio of surface area to solution volume. Does this imply that concentration cells formed in crushed glass and, concomitantly, the solution is not at equilibrium? The correlation of leach rates with reversible thermodynamic terms should be independent of kinetic parameters.

Work by Grambow and his co-workers is based on the equilibrium between crystalline precipitates and solutions to justify the continuously dissolving glasses even in saturated solutions. The glasses may never reach the equilibrium state because of their metastability. The present work uses the equilibrium between glasses and solutions in the calculation of free energy, using a simple fractional addition of each free energy of hydration of glass constituents, or by using bond energy calculation. How can the author justify the continuous glass dissolution in light of the work by Grambow and his co-workers?

In the calculation of free energy of hydration, several aspects need to be considered and justified; if it can be correlated with both the ionic potential and the ionic field strength, it is consequential to take into account the ionic strength of solution. Is the present correlation valid in repository solutions other than DI water? The fractional addition of each free energy of hydration does not explain the mixed alkali effects where the durability of glass does not change linearly following the variation of glass composition. While the free energy of hydration is a fractional addition from that of each component at approximately neutral pH, the correlation at high pH is absolutely empirical. Further, the author does not address the high dissolution at low pH and the time-dependent pH. No glass structure was taken into consideration in the calculation. There are varieties not only of atomic structures but also of microstructures such as phase separation.

In the kinetic formulation; the incorporation of leachant concentration in "reaction constant" (or a reaction kinetics in a broad sense) is absent because the leach rates depend on the leachant concentrations; the mentioned parabolic curve is far from the derived equation (11) which itself is strange due to the double exponential term in temperature expression; the pH dependence on the rate equation is highly empirical; and the precipitation rates do not have any term of activation energy and the factor m (deviation from equilibrium) implies the kinetic control.

Although the work with ancient glasses is appreciated, it may be premature to conclude that waste glasses are durable over geological time. Actually, we need information on material's loss during geological times in ancient glasses in light of NRC regulation of the controlled release rate of radionuclide. Work by Newton and Paul is highly desirable in measuring glass loss in geological time.

In experiments, the author stated the possibility of the involvement of glass powder obtained from glass crushing. This seems to be significant considering precipitation products.

More work is needed in most of the major areas discussed in the report. Areas specifically recommended are as follows:

- The validity of thermodynamic approach should be clarified to be independent of kinetic parameters. For instance, time variation in experiments would be a way to prove it.
- The correlation of glass durability with free energy of hydration should incorporate the mixed alkali effect, solution ionicities, glass structure including atomic- and micro-structures, activity coefficient, and mechanistic pH effect (particularly at low pH).
- Precise and accurate description of the kinetic equation is required, specifically in (1) precipitation rates including activation energy, (2) Arrhenius activation energy of the overall kinetics is of a double exponent term, and (3) the mechanistic pH effect (particularly at low pH).
- In experiments, (1) the monolith and crushed glasses are recommended to be compared at a fixed surface area; (2) solution replenishment or flow rates need to be studied; (3) dating (or materials loss/century) data are more valuable than laboratory test data in ancient glasses; and (4) caution should be given to the contribution of powdered glasses from crushing and are not to be mixed with precipitation products.

RELATED HLW REPORT

1. R.G. Newton and A. Paul, Glass Technology, 21, 307 (1980) has a correlation of free energy of hydration with the thickness loss (mm/century) of ancient glasses.

APPLICABILITY OR DATA TO LICENSING

[Ranking key data(), supporting (x)]

- (a) Relationship to Waste Package Performance Issues Already Identified

- 2.3.2.1.1, which waste form dissolution mechanisms are most likely?
- 2.3.2.1.2, what are the rates of dissolution associated with the potential waste form dissolution mechanisms?
- 2.3.2.2, what non-radioactive dissolution products are likely to be produced from the waste form?
- 2.3.2.3, what are the solubilities of the radionuclides released from the waste form?
- 2.3.2.4, what will be the chemical species of the radionuclides released from the waste form?

Related to ISTP issues

Theoretical Glass durability - a function of glass composition.
a function of glass structure.
a function of test parameters.

Experimental

Leaching test - 55 nuclear waste glasses, and 100 natural and man-made glasses.

(b) Licensing Issues

- Predictive model combining thermodynamic and kinetic approaches.
- The correlation of leaching with free energy of hydration of glass components and pH effect.
- Leaching of ancient glasses.

(c) Comments Related to Licensing

This report provides predictive models and supporting data which need to be better formulated and understood prior to licensing waste package.

ABSTRACT

The long-term durability of nuclear waste glasses can be predicted by comparing their performance to natural and ancient glasses. Glass durability is a function of the kinetic and thermodynamic stability of glass in solution. The relationship between the kinetic and thermodynamic aspects of glass durability can be understood when the relative contributions of glass composition and imposed test conditions are delineated. Glass durability has been shown to be a function of the thermodynamic hydration free energy which can be calculated from the glass composition. Hydration thermodynamics also furnishes a quantitative frame of reference to understand how various test parameters affect glass durability.

Linear relationships have been determined between the logarithmic extent of hydration and the calculated hydration free energy for several different test geometries. Different test conditions result in different kinetic reactivity parameters such as the exposed glass surface area (SA), the leachant solution volume (V), and the length of time that the glass is in the leachant (t). Leachate concentrations are known to be a function of the kinetic test parameter $(SA/V)t$. The relative durabilities of glasses including pure silica, obsidians, nuclear waste glasses, medieval window glasses, and frit glasses define a plane in three dimensional G_{hyd} -concentration- $(SA/V)t$ space. At constant kinetic conditions, e.g. test geometry and test duration, the three dimensional plane is intersected at constant $(SA/V)t$ and the G_{hyd} -concentration plots have similar slopes. The slope represents the natural logarithm of the theoretical slope, $(1/2.303 RT)$, for the rate of glass dissolution.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory for the U.S.
Department of Energy
Contract No. W-7405-Eng-48.

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

Shaw, H. F.
"Plan for Spent Fuel Waste Form Testing for NNWSI."
UCID-21272, November, 1987.

DATE REVIEWED: 12/6/88.

PURPOSE

The purpose of this report is to explain the purposes and objectives of spent-fuel waste-form testing, to give a rationale for studies conducted and quality assurance level assignments, to describe tests, analyses and characterization of spent fuel, to generate models for radionuclide release from spent fuel and to discuss application of results and how test plans support the study plan. "The report is based on the Waste Form Spent Fuel Scientific Investigation Plan (SIP) for WBS element 1.2.2.3.1 for NNWSI. This SIP should be used as a reference document."

"... to address directly...information needs taken from the NNWSI Project Issues Hierarchy (version dated 8/7/86): Issue 1.5, Will the waste package and repository engineered barriers meet the performance objective for radionuclide release as required by 10-CFR-60.113?. 1.5.1 Waste package design features that affect the rate of radionuclide release. 1.5.2 Material properties of the waste forms. 1.5.3 Scenarios and models needed to predict the rate of radionuclide release from the waste package and engineered barrier system. ... the results of the spent fuel activities Will provide data to help resolve information needs 1.4.4, 1.5.4 and 1.5.5 and issues 1.1, 1.4 1.9 1.10 and 1.11. The structure of this ... SIP closely parallels the information needs listed above and the discussion in Chapt. 8 of the NNWSI Project SCP."

KEY WORDS

Planned work, spent fuel, corrosion, oxidation, Zircaloy, stainless steel, uranium dioxide.

CONTENTS

This report consists of 30 pages:

4 pgs.	Title page, Table of Contents, etc.
4 pgs.	Purposes and Objectives
6 pgs.	Rationale for Selected Studies and Quality Assurance Level Assignments
1 pg.	Description of Tests and Analyses, and Previous Work
9 pgs.	Characterization of the Spent-Fuel Waste Form
4 pgs.	Generate Models for Release from Spent Fuel
3 pgs.	Application of Results
2 pgs.	List of Test Plans to Support this Study Plan
3 pgs.	References

AMOUNT OF DATA

This is a test plan. There is no data. There are a number of activities, D-20-(40-52) deal with integration of information, testing, meeting information needs and quality assurance level. Previously issued test plans and additional test plans are listed.

TEST CONDITIONS

Some test conditions discussed in the plan include dissolution rate of irradiated spent fuel, radionuclide release rates from spent fuel, solution chemistry of water in contact with spent fuel and UO_2 in saturated, semi-static and in unsaturated conditions in J-13 water and in deionized water. Other studies involve the oxidation of UO_2 , corrosion tests of cladding, carbon-14 inventory and release rate, developing techniques for test planning and design and generating models. Spent fuel data from vendors, utilities and other sources would be integrated. Referenced tests were conducted on specimens from pressurized water reactors (PWRs) and at ambient hot cell temperatures, 85°C and 25°C in silica reaction vessels with loose-fitting lids and in sealed 304 stainless steel vessels. Tests were conducted on bare fuel, and on fuel with and without defective cladding. Data used will be qualified at Quality Assurance (QA) Level I. Future tests are expected to use Approved Testing Materials (ATMs) provided by the Materials Characterization Center (MCC). Fuels also will include those from boiling water reactors (BWRs) and some stainless steel clad fuel.

UNCERTAINTIES IN DATA

None given by author.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given by author.

CONCLUSIONS OF AUTHOR

None given by author.

COMMENTS OF REVIEWER

This plan coupled with the referenced SCP, addresses many of the questions that need to be considered in any determination of radionuclide release from spent fuel. Since this paper is a plan covering spent fuel, many issues, information needs and activities were cited, and each of these subjects, along with plans concerning it, would warrant a critical evaluation. Integration of information is planned, and quality assurance levels for the data are given.

The details of needed tests related to questions raised were not given, and it is not clear that the planned tests are the only tests needed to answer the questions. More information on the tests probably is available in the Waste-Form Spent-Fuel SIP which is recommended as a reference document.

Some of the ten previously issued test plans relating to spent fuel have been critically reviewed and are in the NIST/NRC data base. There are seven additional test plans listed in the paper and the author states that other test plans will be added as the need arises. It will be evident from reading the reviewer's comments on the test plan in the data base that the tests, while providing useful data, are not sufficient to answer the question they address. An example of this is "Zircaloy spent fuel cladding electrochemical corrosion experiment at 170°C and 120 PSIA H₂O" by H. D. Smith, HEDL-7545. This is a well planned and useful test but does not provide needed electrochemical data.

Test method development through the Materials Characterization Center (MCC) would be useful as well as peer review of planned tests.

RELATED HLW REPORTS

1. Yucca Mountain Site Characterization Plan (SCP)
2. Waste Form Spent Fuel Scientific Investigation Plan (SIP)
3. Wilson, C. N., "Test Plan for Series 2 Spent Fuel Cladding Containment Credit Tests," HEDL-TC-2353-3 (1984).
4. Wilson, C. N., "Test Plan for Cladding Containment Credit Tests," HEDL-TC-2353-2 (1983).

5. Smith, H. D., Zircaloy Spent Fuel Cladding Electrochemical Corrosion-Scoping Experiment," HEDL-TC-2562 (1984).
6. Einziger, R. E., "Technical Test Description of Activities to Determine the Potential for Spent Fuel Oxidation in a Tuff Repository," HEDL-7540 (1985).
7. Smith, H. D., "Zircaloy Cladding Corrosion Degradation in a Tuff Repository," HEDL-7455, Rev.1 (1985).
8. Einziger, R. E., "Test Plan for Series 2 Thermogravimetric Analyses of Spent Fuel Oxidation," HEDL-7556 (1986).
9. Smith, H. D., "C-Ring Stress Corrosion Cracking Scoping Experiment for Zircaloy Spent Fuel Cladding," HEDL-7546 (1986).
10. Smith, H. D., "Zircaloy Spent Fuel Cladding Electrochemical Corrosion Experiment at 170°C and 120 PSIA H₂O," HEDL-7545 (1986).
11. Wilson, C. N., "Test Plan for Series 3 NNWSI Spent Fuel Leaching/Dissolution Test," HEDL-7577 (1986).
12. Einziger, R. E. and Woodley, R. E., "Test Plan for Long-Term, Low-Temperature Oxidation of Spent Fuel, Series 1," HEDL-7560 (1986).

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

- 2.3.1 regarding physical, chemical and mechanical properties of the waste form and how these properties change and alter the ability of the waste form to contribute to the overall performance of the repository system.
- 2.3.2 regarding the solubility of the waste form under potential repository conditions.
- 2.3.5 regarding how corrosion products interact with the waste form.
- 2.3.6.1 regarding predicted rate of failure for failure mechanisms.
- 2.3.6 relating to spent-fuel damage and failure mechanisms.
- 2.3.6.2 regarding predicted size of cladding breach associated with a given failure mechanism.
- 2.3.6.3 regarding how defects alter the retention capability of the spent-fuel waste form.

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Lawrence Livermore National Laboratory for the U.S.
Department of Energy
Contract No. W-7405-Eng.

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

Wilson, C. N. and Shaw, H. F.
"Experimental Study of the Dissolution Spent Fuel at 85°C
in Natural Ground Water."
UCRL-94633, December 1986.

DATE REVIEWED: 8/1/88; Revised 1/7/89.

PURPOSE

To investigate the dissolution of PWR spent fuel in J-13 groundwater after the waste package has cooled enough to permit water to enter a breached container and contact fuel rods which may have experienced some cladding failure.

KEY WORDS

Experimental data, chemical analysis, laser-excited fluorescence, laboratory, air, J-13 water, ambient temperature, high temperature, semi-static, spent fuel (PWR), ^{241}Am , ^{244}Cm , ^{137}Cs , ^{129}U , ^{237}Np , ^{239}Pu , ^{240}Pu , ^{99}Tc , ^{126}Sn , ^{90}Sr , ^{14}C , dissolution.

CONTENTS

The report is eight pages long, containing five figures, five tables, and five references. The test procedures are described briefly, and results are given and discussed.

AMOUNT OF DATA

Table I.: "Test Specimens," lists seven identification numbers used for reporting purposes and a description of each specimen, the reactor, the test series, and the temperature of the run.

Table II.: "Series 3 Solution Iron Concentration," lists the identification numbers for six specimens, and the iron concentration in micrograms per milliliter for periods of 0, 33, 147, and 174 days.

Table III.: "Uranium Release Data (g)," lists for seven specimens the uranium content in periodic solution samples, final solutions, terminal rinse solution, terminal acid strip solution, the total amounts, calculated fractional release, and the percent in solution.

Table IV.: " $^{239+240}\text{Pu}$ Release Data (nCi)," lists for seven specimens the plutonium content in periodic solution samples, final solutions, terminal rinse solution, terminal acid strip solution, the total amounts, calculated fractional release, and the percent in solution.

Table V.: " ^{99}Tc Release Data (nCi)," lists for seven specimens the technetium content in periodic solution samples, final solutions, terminal rinse solution, terminal acid strip solution, the total amounts, calculated fractional release, and the percent in solution.

Figure 1: "Series 3 Test Configuration," is a drawing of the apparatus used for bare fuel tests and for cladding tests.

Figure 2.: "Uranium Measured in Unfiltered Solution Samples," shows the concentration of uranium in micrograms/milliliter (from 10^{-3} to 10^2) plotted against days (from 0 to 240) for seven specimens.

Figure 3.: " $^{239+240}\text{Pu}$ Activities Measured in $0.4\ \mu\text{m}$ Filtered Solution Samples," shows the activities in picocuries/milliliter (from 10^{-2} to 10^5) plotted against days (from 0 to 240) for seven specimens.

Figure 4: " ^{99}Tc Activities Measured in Unfiltered Solution Samples," shows the activities in picocuries/milliliter (from 10^0 to 10^5) plotted against days (from 0 to 240) for seven specimens.

Figure 5.: " ^{14}C Activities Measured in Unfiltered Solution Samples," shows the activities in picocuries/milliliter (from 10^0 to 10^4) plotted against days (from 0 to 240) for seven specimens.

TEST CONDITIONS

Several series of tests were conducted. This report deals with the first cycle of Series 3, and a comparison of the results with Cycle 1 of the Series 2 tests.

Series 3 was conducted at 85°C with J-13 water in sealed 304L stainless steel vessels. The first cycle was terminated after 174 days. Cycle 2 was restarted with fresh well water in new 304L SS vessels.

Series 2 tests were run at 25°C in fused silica vessels.

(1) State of the Material being Tested

Four test specimen configurations were used in both series of tests.

1. Without defects--cladding intact and end fittings water-tight.
2. With hole defects--cladding containing two (≈ 0.01 in. diameter) laser-drilled holes and end fittings water-tight.
3. With slit defects--cladding containing a machined (≈ 0.006 in. by 1 in.) slit and end fittings water-tight.
4. No cladding--bare spent-fuel pellet fragments obtained by splitting the cladding; empty cladding hulls included in the test vessel.

(2) Specimen Preparation

All test specimens prepared from five-inch-long fuel rod sections. Cladding external surfaces were decontaminated to < 50 cps alpha activity to remove any contamination from preparation and handling in contaminated hot cells. Water-tight end fittings were made from stainless steel vacuum adapters with ethylene propylene O-rings to seal against the cladding.

(3) Environment of the Material being Tested,

Tests were run at 85°C and 25°C in sealed 304L SS vessels using J-13 groundwater. The test method was semi-static. Periodically, solution samples were taken and the sample volume (10 to 30 ml) replaced with an equal volume of fresh J-13 water.

UNCERTAINTIES IN DATA

The concentrations of uranium (U) measured in filtered sample fractions are not significantly different from concentrations measured in unfiltered samples, but the laser-excited fluorescence method is not sensitive to U in fine solid particles initially present in unfiltered samples.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

1. Uranium concentrations peaked at higher levels early in the Series 3 bare-fuel tests than in Series 2 tests and fell to much lower levels. Pu activities in the 85°C Series 3 bare-fuel tests also fell to lower levels than in the Series 2 tests.
2. The corrosion products from stainless steel vessels affected solution chemistry in the Series 3 tests; The drops in actinide and Tc concentrations may have been caused by co-precipitation with iron oxy-hydroxide and/or reduced solubility due to reduced oxygen potential.
3. Fuel dissolution behavior in the bare-fuel tests did not depend on temperature (85°C vs 25°C). Vessel type (sealed SS vs unsealed silica) and fuel type (HBR vs TP) appeared to affect concentrations and total measured release values.
4. The chemistry of J-13 well water was little changed at 25°C in both Series 2 and 3 tests, but at 85°C in the Series 3 tests, Ca, Mg, Si, and HCO₃ concentrations were reduced.
5. In both Series 2 and 3 tests, release of radionuclides was much greater from bare-fuel than from fuel with defected cladding.

COMMENTS OF REVIEWER

From this study and related HLW reports it has been concluded that actinide release from spent fuel is a congruent process while fission products such as ⁹⁹Tc are released at a much faster rate, possibly because they are concentrated at the grain boundaries. The reviewer finds the conclusions based on comparisons with other experiments to be very confusing. The authors may state a fact but not really a conclusion. For example, conclusion 5. above cannot possibly be very surprising.

The reviewer recommends that release of radionuclides be compared with the NRC 10⁻⁵ annual release rate limit (based on nuclide inventory after 1000 years of storage). In this report the solution concentration of U and Pu are somewhat below the 10⁻⁵ limit while release of ⁹⁹Tc and ¹⁴C are somewhat above the limit. Thus far tests of this type have been done on 2 reactor fuels. Measurements should be made on additional fuels to determine the variability in spent fuels.

It is clear that the purpose of filtering is to detect the presence of small particulate or colloidal U, but the authors never state a conclusion concerning their importance.

Presence of colloidal material could be of crucial importance because the small particles might also lead to transport of other fission products leading to much higher transport than expected on the basis of solubility data.

It appears that 10^{-5} of the specimen inventory is not rate (per year). The NRC criterion is the 10^{-5} /year, controlled release rate. Therefore, a sample calculation should be given including the time factor.

The solubility limit, which may not be available at the present time, is not given in this paper. Perhaps the solubilities of pure elements in deionized water would be useful if they were drawn in all figures.

Although the curves show the uranium concentration at 25°C levels off with a higher concentration than that at 85°C, the total uranium release in the Series 3 bare fuel tests was ~5 times greater at 85°C than at 25°C as listed in Table III, since the results of Table III took into account solid precipitates. The following two problems need clarification before having a complete scenario of events: (1) Can those precipitates on the test vessel be formed in rock environments? (2) Is, the 10^{-5} , rate (per year) or not?

Figure 1 does not appear to show any gaps, nor to describe maintaining the air gaps in the content, for defected or for bare fuels. Also, the oxygen has a solubility limit in the solution at the level of from ppm to ppb. Therefore, this discussion is valid except one case when the dissolution rate of gaseous oxygen is very fast compared to the rate of iron oxidation with an infinite amount of gaseous oxygen to be supplied. Certainly, a qualitative estimate in the paper would be useful.

The authors list all possible roles of iron ions in decreasing the dissolved uranium concentration. Therefore, the effects of chromium and nickel should be addressed too.

RELATED HLW REPORTS

1. C. N. Wilson and V. M. Oversby, in Waste Management 85, Ed. R. G. Post, Vol. 1, pp. 497-504 (also UCRL-91464, March 1985).
2. V. M. Oversby and C. N. Wilson, in Scientific Basis for Nuclear Waste Management IX, Ed. L. O. Werme (Materials Research Society, Pittsburgh, PA 1986) pp. 337-346.
3. C. N. Wilson, "Results from Cycles 1 and 2 of NNWSI Spent Fuel Dissolution Tests," HEDL-TME-85-22, Hanford Engineering Development Laboratory, Richland, WA.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

- 2.3.2 regarding solubility of the waste form
- 2.3.2.3 regarding solubility of the radionuclides released from the waste form
- 2.3.6.2 regarding ability of defective cladding to retain radionuclides

(b) New Licensing Issues

(c) General Comments

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore Laboratory for the U.S.
Department of Energy
Contract No. W-7405-Eng-48.

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

Wolery, T. J.
"Calculation of Chemical Equilibrium between Aqueous
Solution and Minerals: the EQ3/6 Software Package."
UCRL-52658, February 1979.

DATE REVIEWED: 9/30/88; Revised 10/31/88; 11/5/88.

PURPOSE

"The purposes of this report are to announce the availability of the EQ3/6 software package, to discuss the application of EQ3 and EQ6 to solving problems in aqueous geochemistry, to compare these with other available programs, and to present the mathematical and numerical approaches adopted in program EQ6."

KEY WORDS

Theory, computation development, Monte Carlo, Newton-Raphson, relaxation, reaction path, flow-through model; SOLMNEQ, WATEQ, REDEAL, MINEQL, PATHI, SOLSAT, TOTH, field, simulated field, Salton Sea Water, groundwater, simulated groundwater, pH=3 HCl solution, acid solution (pH <7), ambient pressure, ambient temperature, basic (alkaline) solution (pH >7), high pressure, high temperature, neutral solution (pH = 7), redox condition, static (no flow).

CONTENTS

This report consists of 41 pages which include an abstract, an introduction, a glossary of symbols, 9 tables, 8 figures, and the following number of pages covering each topic listed:

<u>Topic</u>	<u>Pages</u>
Capabilities of Programs EQ3 and EQ6	1.5
Equilibrium calculations in Aqueous Geochemistry:	
Nature of Chemical Equilibrium Problems	1.0
Development of Models for Aqueous Systems	2.0
Applying the Newton-Raphson Method to the class II Equilibrium Calculation:	
Basic Development	13.0
Under-Relaxation Techniques	0.5
Optimizing Starting Estimates	0.5
Finding the Correct Phase Assemblage	4.0
Computing Reaction Path Models:	
Types of Models	1.0
Use of Finite Differences	1.5
The Flow-Through Model	1.0
Example: Dissolution of Microcline	1.5
Example: Heating of Salton Sea Water	5.0
References	3.0
Appendix A. Contents of the EQ3/6 Software Package	1.5
Appendix B. Sample Request Form to Obtain the Package from the National Energy Software Center	1.0
Appendix C. Note on Thermodynamic Data	0.5

TEST CONDITIONS

The author adopted three general steps commonly used in solving a chemical equilibrium problem. They are "(1) to define the model in terms of its physical and thermodynamic nature, (2) to manipulate this original set of equations into a desirable form, and (3) to solve the remaining simultaneous equations."

Many trial and error methods are developed to solve non-linear equations and to determine the system with the best guess based on the limited amount of known input information and numerical solutions.

Particularly in many instances, this work is based on the model developed by Helgeson and his coworkers. Helgeson's program was modified to improve the treatment of (1) supersaturation, (2) drift error involved in the integration of differential equations, and (3) long and costly execution.

EQ3/6 is composed of two separate works, EQ3 and EQ6. "EQ3 computes the concentration, thermodynamic activity of each chemical species, and the saturation state of the fluid with respect to all relevant mineral phases." "EQ6 first equilibrates the input system by calculating a new model of

modified fluid plus precipitates, and then computes reaction progress models of compositional evolution and mass transfer in a closed or open (flow-through) system containing this aqueous solution (with or without any initial precipitates.)"

"Data files support model calculations in the temperature interval, 0-350°C, either at pressures on the 1 atm-steam saturation curve (0-100°C at 1 atm and 100-300°C with the steam saturation) or at a constant pressure of 500 bars."

UNCERTAINTIES IN DATA

"We lack sufficient understanding of these parameters (activity coefficients) at high temperatures and pressures, but the present assumption of unit activity coefficients for such species appears reasonable."

"EQ6 test for convergences by comparing each of $\beta_{\max}$ (the largest residual sector) as $\delta_{\max}$ (the largest Newton-Raphson correction term) with a user-specified tolerance parameter (usually in the range 10^{-6} to 10^{-10})."

DEFICIENCIES/LIMITATIONS IN DATABASE

"The activity coefficient approximations for aqueous species are not suitable to describe aqueous solutions of concentration greater than about 1 molal ionic strength."

"log k values in no way represent a critical and comprehensive compilation, and uncertainties in complex dissociation data are in general much greater than for mineral dissolution data."

Solid solution might be modeled as "ideal solutions, but many are obviously quite non-ideal."

To treat the divergence of Newton-Raphson iteration and the singularity of the ill-condition of Jacobian matrix, special techniques and modification were made. However, "some are specific to the chemical equilibrium calculation dealt with here."

When the maximum precipitable mass of each phase is very small the scaled affinity of the phase is arbitrary reduced. "If a tie exists after scaling the affinities, one must make an arbitrary choice, such as deleting the phase with the lowest numerical index."

"I shall assume that, once a satisfactory phase assemblage has been found, no further question of uniqueness need be considered." However, "it may not be true when some popular non-ideality relations are applied."

In the example of "heating Salton Sea Water", there was a discussion of the realistic appearance of colloid particles or metastable phases.

CONCLUSIONS OF AUTHOR

There is no formal section entitled CONCLUSIONS. The following is quoted from the content as reviewers' conclusion.

"The newly developed EQ3/6 software package computes equilibrium models of aqueous geochemical systems. The package contains two principal programs: EQ3 performs distribution-of-species calculations for natural water compositions; EQ6 uses the results of EQ3 to predict the consequences of heating and cooling aqueous solutions and of irreversible reaction in rock-water systems."

"The calculation predicts in detail the changes in fluid composition, the identity, appearance, and disappearance of secondary minerals, and the values of reaction progress at which the fluid saturates with reactants."

"The methods used in EQ3 have been discussed in detail by Wolery and Waters, and were used in a computer program called SALT. This document therefore concentrates on presentation of the mathematical derivations used in EQ6 and discussion of some of the important numerical techniques adopted."

"The EQ6 uses the Newton-Raphson method to solve the governing equations of chemical equilibrium for a system of specified elemental composition at fixed temperature and pressure. Convergence is aided by optimizing starting estimates and by under-relaxation techniques. The minerals present in the stable phase assemblage are found by several empirical methods. Reaction path models may be generated by using this approach in conjunction with finite-differences. This method is analogous to applying high-order predictor-corrector methods to integrate corresponding set of ordinary differential equations, but avoids a propagation of error."

"The programs are valuable for studying such phenomena as the formation of core bodies, scaling and plugging in geothermal development, and the long-term disposal of nuclear waste."

COMMENTS OF REVIEWER

This report describes methods developed for use in the determination of aqueous geochemical systems. Emphases are on the developing methods to solve non-linear equations and on the empirical methods to determine the system with the best guess based on the limited amount of known input information

and numerical solutions. The author improved existing codes such as those made by Helgeson and his co-workers. He provided many useful methods, including various tricks which often are important for the users and difficult to identify. The following is the reviewer's comments for future study which have not been addressed fully in the content.

"The involvement of kinetics is the issue to be discussed in irreversible reactions. This is particularly important in nuclear waste management where the time frame is very long. The time sequence in precipitation, evaporation, or condensation is a good example. Also, as mentioned by the author too, metastable phases actually do exist. How do we incorporate these phases in the chemical model?"

"There are many unclear and less specific descriptions of chemical reactions. The users may need more specific examples for a better understanding and for finding the applicability of the present methods to their problems."

"The methods are based on trial and error, and are quite empirical. Therefore, they should be organized in a better way for user-specific cases. Sometimes, they are very risky for users. For instance, the divergence of numerical iteration is not necessarily the key criterion to determine the phases present: the divergence can be from other sources as well. Also, there must be ways to prove these methods either experimentally or with the aid of other numerical methods such as the calculus of variation (free energy minimization)."

"Regarding many models of activity coefficients in solid solution and aqueous solute species, the author should be more realistic in choosing those candidates or developing his own models. Too many models were presented without identifying specific advantages to various users' problems."

"Finally, the controversy of system redox should be discussed. There is no system redox in a complex system. How do we deal with individual redox in conjunction with system parameters?"

RELATED HLW REPORT

1. Walters, L.J., Jr., and T.J. Wolery, "A Monotone-Sequences Algorithm and FORTRAN IV Program for Calculation of Equilibrium Distributions of Chemical Species," Comp. Geosci., 1, 57-63, 1975.
2. Wolery, T.J., and L.J. Walters, Jr., "Calculation of Equilibrium Distributions of Chemical Species in Aqueous Solutions by Means of Monotone Sequences," Math. Geol. 7, 99-115, 1975.
3. Viani, B., "Interim Report on Modeling Sorption with EQ3/6," UCID-21308, Revision 1, January 1988.

APPLICABILITY OR DATA TO LICENSING

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

- (a) Relationship to Waste Package Performance Issues Already Identified
 - 1.1.2.3 how and to what extent is local groundwater flow affected by structural, stratigraphic, and lithologic discontinuities and heterogeneities?
 - 2.1.2 what will be the physical characteristics (e.g., temperature, pressure, and flow rates) of the brine reaching the waste package container as a function of time.
 - 2.1.3 what will be the chemical characteristics (e.g., Eh, pH, and chemical composition) of the brine reaching the waste package container as a function of time?
 - 3.1.1.2 what is the present amount of interstitial and bound water and its chemistry in the host rock (intracrystalline and intercrystalline inclusions, hydrous materials) ?
- (b) New Licensing Issues
- (c) General Comments

This report provides methods to predict geochemical environments which need to be better formulated prior to licensing waste package. It is very difficult to determine the geochemical conditions experimentally, because (1) too many chemical and radiational species are involved (2) the time over which the prediction is required is very long, and (3) high temperatures are involved. The present methods provide us with a relatively simple and convenient method to overcome these difficulties analytically including numerical evaluations.

ABSTRACT

"The newly developed EQ3/6 software package computes equilibrium models of aqueous geochemical systems. The package contains two principal programs: EQ3 performs distribution-of-species calculations for natural water compositions; EQ6 uses the results of EQ3 to predict water systems. The programs are valuable for studying such phenomena as the formation of ore bodies, scaling and plugging in geothermal development, and the long-term disposal of nuclear waste.

EQ3 and EQ6 are compared with such well-known geochemical codes as SOLMNEQ, WATEQ, REDEQL, MINEQL, and PATHI. The data base allows calculations in the temperature interval 0-350°C, at either 1 atm-steam saturation pressures or a constant 500 bars. The activity coefficient approximations for aqueous solutes limit modeling to solutions of ionic strength less than about one molal.

The mathematical derivations and numerical techniques used in EQ6 are presented in detail. The program uses the Newton-Raphson method to solve the governing equations of chemical equilibrium for a system of specified elemental composition at fixed temperature and pressure. Convergence is aided by optimizing starting estimates and by under-relaxation techniques. The minerals present in the stable phase assemblage are found by several empirical methods. Reaction path models may be generated by using this approach in conjunction with finite-differences. This method is analogous to applying high-order predictor-corrector methods to integrate a corresponding set of ordinary differential equations, but avoids propagation of error ("drift")."

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory for the U.S.
Department of Energy
Contract No. W-7405-Eng.

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

O'Connell, W. J. and Drach, R. S.
"Waste Package Performance Assessment: Deterministic
System Model Program Scope and Specification."
UCRL-53761, 1986.

DATE REVIEWED: 8/22/88; Revised 10/31/88; 11/5/88.

PURPOSE

"We describe the principal processes affecting the waste package's long-term performance and the models developed for these processes." The report also includes the identification of the principal processes.

KEY WORDS

System performance computer code, Monte Carlo, general corrosion, pitting, solubility, Radiation Model, Thermal Model, Mechanical Model, Waste Package Environment Model, Waste Form Alteration Model, Waste Transport Model, System Drive Model, TACO2D, ORIGEN2, WAPPA, TOUGH-A, MORSE-L, field, Yucca Mountain, air, tuff composition, Cl, tuff, alpha radiation field, gamma radiation field, ambient temperature, ambient pressure, lithostatic pressure, cladding, stainless steel, weld, spent-fuel-rod without defects, glass (not specified), high-level-waste (not specified), spent fuel (not specified), actinides, fission products, neutron, gamma rays (not specified), density, modules of elasticity, thermal conductivity, thermal expansion, yield strength, corrosion (general), deformation (elastic), leaching (radiation enhancement), leaching (spent fuel), matrix dissolution (glass).

CONTENT

This report consists of 52 pages which include an executive summary, an abstract, an introduction, a list of contents, a

list of figures, 21 figures, a list of tables, 9 tables, a glossary, and the following number of pages covering each topic listed:

<u>Topic</u>	<u>Pages</u>
Waste Packages and Processes Affecting Waste Package Performance:	
Waste Forms and Waste Packages	0.5
Processes Affecting the Waste Package	2.5
Earlier Programs of Similar Scope	2.0
PANDORA Models Description:	
Waste Package Model	0.5
Radiation Model	6.5
Thermal Model	3.0
Mechanical Model	4.5
Waste Package Environment Model	2.5
Corrosion Model	1.0
Waste Form Alteration Model	2.0
Waste Transport Model	0.5
Drive Model	8.5
Conclusions:	1.0
References:	1.0
Appendix A. WAPPA's Gamma Ray Attenuation Model	2.0
Appendix B. PANDORA's Gamma Ray Dose Model	4.0

AMOUNT OF DATA

There are 10 schematics of waste package, 9 flow diagrams, one temperature versus the radius of waste package, a schematic of water flow patterns, 6 lists of elements of data diagrams, and 3 lists of elements of mechanical model.

The dimension of the presented data are:

Gamma Ray Flux (Photons/sec·Cm²) (0 to 5 x 10⁶) versus container Radius (Cm) (0 to 30).

Effective Gamma Ray Absorption Coefficient (m²/kg) (0 to 1.6 x 10⁻²) versus Gamma Ray Energy (MeV) (0 to 1.2).

TEST CONDITIONS

The present system modeling is based on the existing code, WAPPA, developed earlier in the ONWI program. There are modifications for the application of this code to the NNWSI waste package. "The model geometry for an appropriate degree of simplification has essentially one dimension of variation, the radial direction in a cylindrical geometry."

"Each annular element in the waste package is described by its inner and outer radii and a materials name.: Besides the component annuli, the PANDORA adds corrosion-layer annuli, a gas gap annulus and Zircaloy cladding as an additional barrier protecting the spent fuel waste form."

"The properties of waste-form annuli may be space-averaged properties, actual properties of the solid waste form, or total quantity per waste package," depending on each submodel.

"There are seven process models: (1) radiation model, (2) thermal model, (3) mechanical model, (4) waste package environment model, (5) corrosion model, (6) waste form alteration model, and (7) waste transport model. Each model may consist of several interacting or mathematically related submodels. The driver model treats the interactions of the models and the sequencing of these interactions."

Radiation Model

The source model uses code ORIGEN2 which has been developed for the burnup calculation of nuclear fuel, and "interpolates in the time variable."

The gamma ray dose model uses "MORSE-L which calculates radiation transport using a Monte Carlo method."

"The gamma ray absorbed dose rate at waste form surface assumes that the outer-most waste form annulus is a thick self-shielding source and the dose rate at its outer surface comes from that source alone."

"The mass energy-absorption coefficients between 0.4 and 1.0 Mev are nearly equal for main constituents of glass and metal barriers, and that for spent fuel is dominated by the major constituent, uranium by weight."

"The alpha particle dose model gets the alpha particle generation rate from the radiation source model."

"The fission dose model functions similarly to the alpha particle dose model."

Thermal Model

"The model assumes steady-state radial heat transfer, cylindrical symmetry and homogeneous material within an annulus."

Mechanical Model

"The principal elements are waste forms and metal barriers. Other element types account for corrosion and gaps. The elements are assumed to be free to expand in the axial direction."

Waste Package Environment Model

"The simplified model assumes that all the water flux passing through a certain area above the waste package will flow into the emplacement hole and contact the waste package. However, the likely flow at an emplacement hole is around the hole rather than into the hole. After the water's influx to the emplacement hole, we simply assume that the water can keep part of the package wet."

Corrosion Model

"The first-generation corrosion model considers general corrosion in two environments: (1) air-steam, and (2) air-water vapor."

Waste Form Alteration Model

"We assume that activation products contained in the cladding material or stainless steel and Inconel components are converted into mobile form congruent with the corrosion, except for zirconium and nickel."

"We assume that matrix dissolution rate is the limiting factor for the contained elements' release rate. We condense all of the fast-release fraction of a fuel rod, which may actually be released over several years, into its first year after the full rod cladding fails."

"For the matrix-limited component of waste release, we assume that this release begins at its full rate when the first fuel rod cladding is breached. This assumes that the release is limited by water flow and/or matrix solubility rather than the fraction of the fuel rods exposed to the water flow."

"For radionuclides with a fast-release fraction of x %, we assume that the last x % of the matrix has none of this nuclide, and the first (100-x) % has a concentration of this nuclide determined from the total inventory of the nuclide divided by the total inventory of uranium."

"For a glass waste form, it is assumed that release of all elements is controlled by the matrix alteration rates."

Waste Transport Model

"It is assumed that the water flux out equals the water flux in and that any gases mobilized after the first breach are immediately available for transport beyond the boundary of the waste package."

UNCERTAINTIES IN DATA

Radiation Model

"The gamma ray dose model has a reasonable degree of accuracy and additional MORSE-L runs must be performed to explore the degree of accuracy achievable."

"A threshold gamma ray energy is perhaps 0.2 Mev for glass waste forms and 0.3 Mev for spent fuel. Below the threshold gamma ray energy, a high probability of absorption takes place."

"Thermal model can compare limited variations in waste package design where heat transfer is altered."

DEFICIENCIES/LIMITATIONS IN DATABASE

Radiation Model

"The gamma ray dose model has some limitations in accuracy compared to the full situation because of the simplifying approximations we use:

1. Mass energy-absorption coefficients for materials across a range of atomic numbers are not quite equal.
2. The sources are thick but not infinitely thick: a small effect of radius was noted.
3. Some waste form shapes are only coarsely approximated by a cylinder.
4. Spent fuel in the form of fuel assemblies could have some streaming effect in the open channels between rows of fuel rods. It is nonuniform scattering with a spatial variation."

Thermal Model

"If the waste package design departs from cylindrical symmetry and homogeneous material within an annulus, 2-D or 3-D models are necessary. For a horizontally emplaced waste package, the k_e/k ratio is greater than or equal to one, and is not continuous."

"Mechanical model did not evaluate (1) fallen rocks on the horizontal waste package, (2) pinhole penetration through fuel rods which can heat the water intruded exerting an interior pressure, (3) stresses associated with individual rod, and (4) inter-rod forces. The maintenance of cylindrical symmetry is an uncertain assumption when the yielding is significant. Finally, fracture criteria for ductile materials are not of use."

Corrosion Model

"The PANDORA model will take conservative envelope of the sensitivity and localized corrosion modes."

Waste Form Alteration Model

The element release rate did not take into account the constraint imposed by solubility limit. The total release for a group of containers will be deferred to future work.

Waste Transport Model

"Transport is to the borehole wall and future work includes that at some distance into the rock."

CONCLUSIONS OF AUTHOR

"We have developed the first generation of conceptual models for the long-term performance assessment of a nuclear waste package to be emplaced in a repository in an unsaturated tuff environment. The models of the processes and their interactions provide the specification for a first-generation computer program. The purposes of the first generation development are (1) to guide later generations of development and (2) to get first-approximation results examining interactions among the processes and evaluating proposed designs.

Our conceptual models use present knowledge and indicate an agenda for future information needs.

The radiation source model is a standard one and is implemented by data tables from a detailed model. Our gamma

ray attenuation model is a new approximation of a well-understood but complex process. The goals of the approximation are simplicity and reasonably accurate results in variations or sensitivity analysis. We will need to do validation of this approximation.

Our thermal model uses steady-state heat transfer to determine the temperature field. Earlier studies using a time-varying heat transfer code have shown only small departures from the steady-state results.

The mechanical model uses well-understood principles for the elastic stress-strain range and somewhat conservative models for the limits of elasticity and for failure modes.

Future needs in the radiation, thermal, and mechanical areas include modeling of effects near the ends of the waste package, validating simplified models and evaluating the achievable values in the simplification/accuracy trade-off.

The waste package environment excludes liquid water in early years after repository closure, when the local temperature is above the boiling point of water. The groundwater flow details near the waste package are presently unknown for the proposed emplacement geometry and the unsaturated, thermally changing conditions. We have greatly simplified model the which in conservative, possibly by orders of magnitude.

We include general corrosion in the first model, but defer localized corrosion modes such as pitting and stress corrosion cracking. It is unclear whether we can model these modes by establishing conservative bounds on go/no-go thresholds or whether we will need models including microscopic initiation and subcritical growth over the long time period of interest to waste package performance.

Waste form alteration and transport of waste to the waste package boundary are modeled by data tables to be developed from experiments. When the details of groundwater movement through a partially degraded waste package are developed, the corresponding responses of waste form alteration and waste transport processes may require more detailed models to describe the range of possible flow patterns and responses.

Our first generation computer code will be able to examine the interactions of processes affecting the waste package. Interactions among heat source, heat transfer, fluid flow, mechanical stress, and general corrosion are included in the first-generation model. Gamma radiation effects on corrosion can be included via data tables. The magnitudes of different radiation types-gamma rays, alpha particles, spontaneous

fissions, and neutrons--will be calculated over time; their relative magnitudes can guide modeling of their effects in later generations of the model. The first-order effects of progressive degradation of barriers upon fluid flow will be calculated. The effects of fluid flow, temperature, and radiation upon waste form alteration and waste transport to the boundary of the waste package will be calculated.

Calculations with the first-generation computer code will quantify some (but not all) of the important consequences of design choices. Calculations will also indicate which processes and interactions modeled are most important. Calculation of magnitude of effects, sensitivity, and estimates of uncertainty or suspected bias (hopefully in a conservative direction) can identify present model simplifications most in need of refinement in the next generation model."

COMMENTS OF REVIEWER

This report outlines the framework of computer codes for the deterministic system's performance of waste package, based on the existing code, WAPPA, developed earlier in ONWI. It has minor modifications of WAPPA made for NNWSI projects. The system code has to be developed for the requirement of NRC regulations and this work is certainly a unique basis and reasonably written for this purpose. Although the authors insist that the code is intentionally simplified to develop the underlying framework, there are many areas of inconsistency, incompatibility, omissions, inefficiency, and wrong or vague descriptions of the framework itself. Much more work is necessary in the future and it is prudent to wait for the real implementation.

The present code, PANDORA, is a weakly modified version of the WAPPA code for NNWSI projects. They discarded the performance of backfill, included groundwater input data containing gas release and the treatment of spent fuel. However, the underlying framework has not progressed much. Rather, it discarded important issues treated in WAPPA, even though they are considered to be important in NNWSI environments. Those issues include: (1) container oxidation in air/steam conditions, (2) gamma ray attenuation model (will be discussed more below), (3) stress corrosion cracking and creep of containers, and (4) glass leaching.

Also, when each model adopts the existing relevant codes, the authors did not evaluate the basic assumptions used in those codes and their applicability in NNWSI. For instance in code MORSE-L or ORIGEN-2, cross-section track or geometric effects

were neglected, which may be important in NNWSI. The most serious one is the effect of time scale since ORIGEN-2 or MORSE-L are based on the short-term performance. Therefore, the existing codes may not be able to be used when the alteration of waste package or of environments is significant. Neither WAPPA nor the current code provides specific prescriptions for time-dependent boundary conditions such as cracked glasses, plastically deformed containers, breached containers and time-dependent rock temperature. In these circumstances, currently quoted submodels are also considered to be no longer applicable. Such examples are rigorous description of elastic stresses, heat transfer or stress relief in the deformed waste package.

As a first approximation, thermal or mechanical models are unnecessarily extensive, while corrosion models, waste transport models or waste package environment models are too simplified.

The code PANDORA is based on the deterministic model of waste package performance. However, there are codes available based on probabilistic model (the Aerospace Corporation, 1985) or on the combined model with deterministic and probabilistic approaches (Commissariat à l'Energie Atomique and Ecole Nationale Supérieure des Mines de Paris, 1988). Each approach has its unique advantages in licensing the waste packages. Therefore, it is desirable for the authors to compare their approach with the probabilistic one.

More detailed comments are given about each model below:

Radiation Model

Radiation source is presumed to be a line source. This is only valid when the observation distance is far from the source. The current model does not consider radiation far away in rocks from the waste package but the space between bore-hole wall and the waste package which is a very short distance for the use of line source assumption.

Z - defined as the depth such that the attenuation of the primary gamma ray flux from the equivalent line source to the point of observation) is simply a monotonically increasing function of the radius of waste package while the radiation flux is inversely proportional to the sum of Z and the distance of observation (according to reactor-shielding design). Therefore, WAPPA's description is correct.

The assumption of the uniform waste form misleads many conceptually defined quantities such as Z or L" (half of the gamma ray energy existing in the waste form surface originates

from the zone within a depth L" from the surface). During the manufacturing of the waste package, glasses are cracked and those quantities, therefore, may need to be modified accordingly.

Descriptions are needed for the treatment of activation products, decay daughters, prior accumulation of radionuclides to the emplacement of waste packages, alpha- and gamma-radiolysis, radiation embrittlement, and dose-rate effect.

Thermal Model

There are heat losses which were not considered in the model. Examples are heat of vaporization (or condensation) or heat loss through the fractured rock.

Many constants used in the formulation are dependent on temperature and radiation field. They include thermal conductivity, rock temperature, gas or liquid density, volume expansion coefficient, viscosity, and active length of waste form.

Mechanical Model

Descriptions in the plastic regime should be explored. Creep deformation can take place for many years at low stress levels.

Both compressive and tensile stress concentrations can be present from waste package geometry and weldments. They are not necessarily associated with existing precracks.

Many equations were described incorrectly in the elastic regime. For instance, equations 3.4-12 and 3.4-16 will also lead to three directional displacements, and equations 3.4-12, 3.4-16 and 3.4-34 use incorrect definitions.

Any fracture taking place may lead to new stress to adjacent components or parts by building stress concentration as far as the stresses of the whole system are reduced. It does not necessarily relieve all the local stress concentrations.

Many elastic constants may also depend on radiation field or temperature. An example is the modification of Young's modulus by radiation embrittlement.

Waste Package Environment Model

More dangerous species are present in groundwater other than chloride ions. They are fluoride ions, carbonate (or bicarbonate) ions, and radicals generated by radiolysis.

Also, solution pH is a time-dependent quantity as glasses interact with water and radiation field.

Corrosion Model

Very little effort is given to model localized corrosions. Also, there are unmentioned failure modes such as salt-cracking, microgalvanic corrosion, wet-dry cycle effect, and inside oxidation of container.

Waste Form Alteration Model

The containers may age for extended periods. For instance, carbides may continuously grow or containers may slowly become embrittled by radiation.

Displacement damage in the waste form has not been ruled out based on a technical assessment from the dominance of thermal crack. It may lead to a significant alteration of the radionuclide transport model.

It is encouraging to have a distribution of container pits. However, the subsequent release modes of radionuclide will vary significantly due to the distribution.

Waste Transport Model

To describe the waste transport properly, it is necessary to include leach models, or, at least, justifications are necessary stating that solubility limit, diffusion, or flow rate is a dominant factor controlling the release rate of the waste form. There are many realistic models in waste transport which are available and recommended.

Drive Model

The model describes every event from the beginning, making a gigantic code. It may be desirable to have a subroutine to pick up necessary models to consider in a given time interval. In this way, the system will be organized more efficiently.

Once any failure occurred, there was no time delay. This seems to be too conservative. For many instances, it takes a while to achieve such a condition. For example, the situation of a single pin-hole is quite different from that of a complete breaching of a container in waste form release. It is hard to believe in the complete instantaneous breaching of a container.

Direct reversible directions (figure 3-14) are confusing since those reversible modifications are also made by the system-loop.

RELATED HLW REPORT

1. INTERA Environmental Consultants, Inc., WAPPA: A Waste Package Performance Assessment Code, Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, OH, ONWI-452 (1983).
2. Boyars, C., Fuller, G., Moller, R., Stephens, K., and Zarembra, L., "Demonstration of Methodology for Waste Package Performance Assessment," The Aerospace Corporation, WPR-86(6810-01)-01, (1985) and related reports.
3. Lewi, J., Mejon-Goula, M. J., Goblet, P. and Cernes, A., Berlin Conference

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

- 2.1 when, how, and at what rate will brine penetrate the packing around the waste package and contact the container?
 - 2.1.3.1 how will the chemical characteristics of the brine reaching the waste package container be affected by radiolysis?
 - 2.1.3.2 how will the chemical characteristics of the brine contacting the waste package container be affected by chemical reaction with the packing and container materials?
- 2.2.1 what will the physical properties of the waste package container materials be as affected by temperature, radiation, interaction with the packing materials, brine migration, and other effects?
- 2.2.2 what will the chemical properties of the waste package container materials be as affected by temperature, radiation, interaction with the packing materials, brine migration, and other effects?
- 2.2.3.1.1 what will be the magnitude of the lithostatic/hydrostatic loads on the waste package container and the resultant stress developed within the container as a function of time?
- 2.2.3.1.2 what will be the magnitude of the thermal stresses developed within the waste package container as a function of time?
- 2.2.4.1 what are the rates of corrosion as a function of time for the various corrosion modes of the waste package container?

- 2.2.4.2.1 what is the predicted rate of radiolytic generation of hydrogen, oxygen, and other species due to gamma radiation in the vicinity of the waste package container?
- 2.2.5 what are the anticipated physical dimensions of waste package container breach as a function of time?
- 2.2.6 what will be the physical characteristics (e.g., temperature, pressure, and flow rates) of the brine penetrating the waste package container and reaching the waste form as a function of time?
- 2.2.7 what will be the chemical characteristics (e.g., Eh, ph, and chemical constituents of the brine penetrating the waste package container and reaching the waste form as a function of time?
- 2.2.8 how will the design of the waste package container accomodate all potential natural and waste package-induced conditions?
- 2.3.1 what are the physical, chemical, and mechanical properties of the waste form, how do those properties of the waste form change with time, and how will such changes alter the ability of the waste form to contribute to the overall performance of the repository system or impact the performance of other barrier materials and properties of the site?
- 2.3.2.4 what will be the chemical species of the radionuclides released from the waste form?
- 2.3.5 how will packing, container materials (including overpacks, canisters, and any special corrosion-resistant alloys or spent fuel rod cladding, if applicable) and/or their alteration products interact with the waste form to cause its alteration and/or effect release of radionuclides?
- 2.3.6.1 what is the predicted rate of failure of each of the potential failure mechanisms for spent fuel.
- 2.3.6.2 what is th predicted size of cladding breach associated with each of the potential spent fuel cladding failure mechanisms?
- 2.4.1 what will be the convective flows in the waste package as a function of time?
- 2.4.3 how will the radionuclide species (i.e., particles, colloids, and solubles) change with time in the waste package?

(b) New Licensing Issues

(c) Comments Related to Licensing

This report provides a predictive computer code of waste package performance which need to be better formulated prior to licensing waste package.

ABSTRACT

"Integrated assessments of the performance of nuclear waste package designs must be made in order to qualify waste package designs with respect to the containment time and release-rate requirements set by the NRC in the Code of Federal Regulations (10 CFR 60). PANDORA is a computer-based model of the waste package and the processes affecting it over the long term, specific to conditions at the proposed Yucca Mountain, Nevada, site. The processes PANDORA models include: changes in inventories due to radioactive decay, gamma radiation dose rate in and near the package, heat transfer, mechanical behavior, groundwater contact, corrosion, waste for alteration, and radionuclide release. The model tracks the development and coupling these processes over time. The process models are simplified ones that focus on major effects and on coupling. This report documents our conceptual model development and provides a specification for the computer program. The current model is the first in a series. Succeeding models will use guidance from results of preceding models in the PANDORA series and will incorporate results of recently completed experiments and calculations on processes affecting performance."

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Lawrence Livermore National Laboratory for the U.S.
Department of Energy
Contract No. W-7405-Eng-48.

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

Russell, E. W., McCright, R. D., and O'Neal, W. C.
"Containment Barrier Metals for High-Level Waste Packages
in a Tuff Repository."
UCRL-53449, October 1983.

DATE REVIEWED: 1/15/89.

PURPOSE

To select candidate metals for the containment of nuclear waste.

KEY WORDS

Data analysis, literature review, scoping test, elongation, tensile strength, yield strength, ductility, corrosion (crevice), corrosion (general), corrosion (intergranular), corrosion (pitting), corrosion (stress cracking) SCC, hydrogen embrittlement.

CONTENTS

26 pages, 4 figures, 10 tables, and 17 references.

AMOUNT OF DATA

No new data. All data taken from the literature. These data consist of 1) a summary of the waste package environment, 2) composition of 17 candidate metals, 3) deterioration rates for several mechanisms of 17 candidate metals, 4) relative costs of 17 metals, 5) mechanical and weldability properties of 17 metals, ranking of 17 metals considering corrosion resistance, mechanical properties, weldability, and cost.

TEST CONDITIONS

No testing conducted.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

"The results of our analysis show the five metals that best satisfy the requirements for disposal of high-level waste at the NNWSI-posed repository at Yucca Mountain. Testing is presently planned or in progress on these metals for further development of the waste package design for the unsaturated zone. The reference canister and overpack metal is AISI 304L stainless steel, but alternative metals will also be considered for reasons previously discussed. The primary alternative metals have been selected from the list of the 17 candidate metals discussed in this report. They are AISI 321, AISI 316L, Incoloy 825 for canisters and overpacks, and 1020 carbon steel for borehole."

COMMENTS OF REVIEWER

This is the first report summarizing the procedure used in selecting five metals, out of seventeen that were considered, for laboratory testing as candidates for nuclear waste container. At this stage, copper and copper alloys were not included in the list of seventeen metals evaluated. The report does not discuss the methods used in arriving at weighing factors for each of the properties considered.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

- 2.2.8 How will the design of the waste package container accommodate all potential natural and waste package induced conditions?

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

Five metals that best satisfy the requirements for use as high-level waste containers were chosen. The reference canister and overpack metal is AISI 304L, and alternative alloys are AISI 321, AISI 316L, Incoloy 825, and 1020 carbon steel for borehole liners.

Appendix C. Waste Compliance Plan for the West Valley
 Demonstration Project High Level Waste Form,
 WVDP-055 West Valley, New York, 1986

Appendix C

NIST Comments on Waste Compliance Plan for the West Valley Demonstration Project High Level Waste Form, WVDP-055 West Valley, New York, 1986

Introduction, pages 1-2.

The composition of the WVDP reference glass in Table I has a wide range of some of the constituents. The range given in this compliance plan may be too broad and needs further explanation based on available leaching data. The effects of variation in the chemical composition of various constituents is needed, especially the effects of Al_2O_3 , SiO_2 , and Fe_2O_3 .

It would be useful to check the glass compositions in the latest version of the WVDP compliance plan. The MCC has done various studies on the effects of composition on leachability of the glass. The ATM-10 reference glass composition is given in Table III on page 10. The ATM-10 reference glass has been shown to be more durable than the CTS (Chemical Test Standard) glass from the WVDP. The Materials Characterization Center (MCC) data on ATM/WV-205 (ATM/WV-205 is a doped version of ATM-10) indicate that this glass falls within target specifications (ref. NUREG/CR-4735, Vol. 4, pages 22-66). The CTS glass also fell within target specifications, but it was less durable than the ATM-10. The CTS glass may not be considered further for use.

1.3 Specifications for Radionuclide Release Properties, pages 16-23.

More explanation of radionuclide release is needed. For example, how does this release correlate with an element like boron that is analyzed and taken as a conservative indicator of other elemental release. This topic may not be appropriate for the WCP, but maybe it should be given greater detailed treatment in the WAPS. That document did not give anything on this subject, so we wonder what DOE is doing to determine what requirements are needed on rate of radionuclide release for the glass compositions proposed to date.

3.9 Chemical Compatibility Specification, pages 49-52.

The compliance plans should specify the service life and requirements for 304 stainless steel canisters. The canister is expected to be given zero credit in a repository and yet it must

be known whether these canisters will serve adequately during the period preceding repository emplacement in a repository container. Questions include how long the canister will be open and will the temporary closure be leak tight according to ANSI 14.5-1977. Information relating to storage times, environmental conditions and required life of the canister is needed.

More detail is needed regarding localized corrosion. Canister heating, due to the pouring of the waste glass and to the subsequent cooling, can affect microstructural phases in the stainless steel. This is likely to result in increased sensitivity to stress corrosion cracking and other forms of corrosion. The 304 stainless steel can be subject to pitting or other local attack if any water is present.

3.12 Drop Test Specification, page 57.

The WVDP should be correlating drop-test studies with other drop-test and glass-fines-release studies that have been conducted by the MCC. The Materials Characterization Center (MCC) has conducted drop tests on glass filled canisters for the Transportation Technology Center (ref. NUREG/CR-4735, Vol. 4, pages 20-21).

Mechanical damage to the canister occurs as a result of rough handling or dropping. Correlations are needed to establish the relation between mechanical damage and expected service life, based on estimates of the effects of mechanical strain on fracture and corrosion performance.

4.1.2 Test Program, page 66.

The Waste compliance schedule is given on page 66. MCC reports indicate that the release rate testing is on schedule.

Appendix D. Consultation Draft Site Characterization Plan
(CDSCP) for Yucca Mountain

APPENDIX D

The NIST reviewed the Consultation Draft Site Characterization Plan (CDSCP) for Yucca Mountain, and developed sixteen critical comments for consideration by the DOE. These were submitted to the NRC.

The Site Characterization Plan (SCP), became available for review in January 1989. NIST found that thirteen of the sixteen critical comments submitted in 1987, had been implemented. In addition, three were partly implemented or not implemented at all. The 1989 review of the SCP resulted in development of eight new comments. In addition, the three from 1987 were reworded and resubmitted. The following is a brief summary of these eleven comments and questions.

EIGHT NEW SCP COMMENTS SUBMITTED BY NIST

Section 7.4.2.6.4 Activities to Determine Transgranular Stress Corrosion Cracking Susceptibility

Comment

Investigations into the stress corrosion cracking behavior of the container alloys seem to be assuming that the container surface will be either homogeneously dry or homogeneously wet, but in the corrosion model (7.4.5.4.6) it is stated that "the waste package will most likely not be uniformly wet."

Section 7.4.3.2 Glass Waste Form Performance Research

Comment

Grouts, cements, and organic materials used in the repository may change the local pH of the repository and affect the local leach rates of radionuclides and the corrosion of the metal waste containers.

Section 7.4.5.4.5 Waste Package Environment Model

Comment

The effects of air flow on the corrosion of the metal canisters is not considered.

Section 7.4.5.4.6 Corrosion Model
7.5.4.6 Metal Barriers

Comment

The term "uniform corrosion" is misleading. "Uniform corrosion" implies the same corrosion rate over the entire surface of the canister. In the SCP, there is no information on the degree of surface roughness. Surface roughness develops gradually on an originally smooth metal surface undergoing general corrosion.

Section 8.3.5.9.2.1.1 Subactivity 1.4.2.1.1

Comment

The composition of the peer review panel is very important. These seven individuals should be recognized as being among the top experts in metallurgy and materials science in the United States.

Section 8.3.5.9.3.2.7 Subactivity 1.4.3.2.2: Transgranular Stress Corrosion Cracking

Section 7.4.2.6 Pitting Corrosion, Crevice Corrosion, and Transgranular Stress Corrosion Cracking

Question

In these sections and throughout the SCP is there an assumption that stress corrosion crack propagation results from anodic dissolution and removal of metal from the crack tip?

Section 8.8.5.9.3.2.7 Transgranular Stress Corrosion Cracking

Comment

In the SCP, the implication is made that by going from the saturated zone to the unsaturated zone of the repository, the uncertainties with respect to corrosion are reduced.

Section 8.3.5.10.2.1.1 Dissolution and Leaching of Spent Fuel

Question

Does the proposed SCP test for rate of release of radionuclides from spent fuel in J-13 water take into

consideration the effect of ground water contamination by container metal ions, or the possible concentration of J-13 salts in the repository?

THREE CDSCP COMMENTS RESUBMITTED BY NIST

Section 8.3.5.9.1 Information Need 1.4.1: Waste Package Design Features that Affect the Performance of the Container.

Comment

The comment given below was addressed in DOE response, #74. The DOE response was not sufficient. While much useful information can be gained from the use of existing ASTM standards and from interactions with ASTM committees, the ASTM is a consensus group, and stricter standards are needed for some aspects of 1) test methods and 2) materials durability for materials used in nuclear waste storage. The comment stands as originally stated. "There is no description of the development and use of standardized test methods that have undergone peer review."

Section 8.3.5.9.1.1.4 Subactivity 1.4.11.4: State of Stress in the Container

Comment

The DOE responded to our comment #77 on the possible influence of corrosion on the state of stress in the container by including pitting and localized corrosion. However, the DOE elected to neglect general corrosion in their calculations, and the justification given for neglecting general corrosion is insufficient. As a result, this point should be considered.

Section 8.3.5.9.2.2.1 Assessment of Degradation Modes in Copper-Based Materials

Comment

DOE claims that it has accepted comment #80, which stated that the scientific basis for degradation modes of copper-base alloys in the CDSCP is not in agreement with scientific literature. In reality, the text in Section 8.3.5.9.2.2.1 has not been changed.

APPENDIX E. The Materials Characterization Center

APPENDIX E. The Materials Characterization Center

A. Program Administration

The manager of the MCC changed on July 1, 1988, and G. B. Mellinger was appointed to this position. G. B. Mellinger attended the WVDP High Level Waste (HLW) Form and Process Testing Integration meeting on July 28-29 in West Valley, NY. The manager and J. E. Mendel met with persons from Lawrence Livermore National Laboratory in August for programmatic discussions. The Statement of Work (SOW) was submitted to WVDP for review. The Technical Program Plan (TPP) was submitted to the OFSD in August for review and in revised form to the Materials Integration Office (MIO) for review in November. Mssrs. Mellinger and Mendel attended meetings in September in Washington, DC regarding Savannah River waste compliance and also had discussions at DOE/HQ concerning the OFSD work. The MCC manager attended the Waste Management Center Second Workshop on Leaching Tests in October in Oak Ridge, TN. Revised drafts of support to the Savannah River Laboratory (SRL) were submitted to SRL for review.

B. Quality Assurance

Some corrective actions were taken and completed as a result of DOE-RL/DOE-HQ audit EA-8801.

A PNL internal audit was held on Sept, 6 and 7. There was an observation that it was not evident that service groups transmitted supporting documents associated with MCC SOWs to the Records Center. Corrective action was taken.

A WVDP audit was held in October, and the MCC QA program was considered adequate and effective. Two findings, one related to a test procedure and the other to a service organization's calibrations, were reported. Five observations were reported relating to test procedures, data corrections, measurement and test equipment calibration and reporting of significant figures.

Surveillance of the impact testing of DWPF canisters indicated that this work went well. Strain circle analysis was revised to include traceability to the SOW and laboratory record books were revised to provide traceability of photographic film to the impact test canisters.

Surveillance of personnel qualification records for persons using the D-cell gamma scan and fission gas sampling procedures and for persons preparing glass per MCC-TP-2 were adequately documented.

No deficiencies were found in the ATM-5 and ATM-6 reference glass archiving, in the cutting of two ATM-104 samples for transfer to the Post Irradiation Testing Laboratory for ceramography or in analytical work on spent fuel characterization. Deficiency report activity involved miscommunication and the interruption of leach testing. The test was restarted and data will be evaluated. In another deficiency report, the operator misunderstood instructions and did not make a void volume measurement for one fuel rod. Void volume will not be reported for this rod. Void volume is so small that it does not affect the calculated results of the fission gas quantity.

Plans were developed for training personnel. Three new staff members were trained and fifteen staff members attended two briefing sessions.

Records supporting the Canister Impact Test results were prepared and transmitted to the SRL. Historic records supporting ARM-1 D-5 and D-6 data will be included with the MCC records at the PNL Records Center. Analytical test results supporting the D-5 package were sent to the Records Center.

C. Support to the Office of Facilities Siting and Development

Analytical Methods

The second waste glass analytical round robin is in progress. Reference solution samples and powdered simulated waste glass containing 2 wt. percent of depleted uranium were mailed to the off site participants. Data have been received from eight laboratories. Three additional laboratories have yet to respond. Planning is underway for the next Analytical Methods Workshop to be held January 17-18, 1989.

Spent Fuel Operations

The ATM-104 fuel rod to be characterized this year was fission gas sampled and sectioned into analytical, archival and test specimens. There was no problem in collecting the fission gas. Gamma scanning takes three days per rod with the detector being used, and fission gas sampling requires one week per rod. In two previous rods, no fission gas was

found, and it was decided that this could have resulted from a defective rod or operator error. A rod from ATM-106 (moderately high burn up and high fission gas release) and from ATM-108 (contains gadolinia, Gd_2O_3 , burnable poison in bundles CZ346 and CZ348 from the Cooper BWR). Fission gas analyses from fuel rods show that relative amounts of xenon and krypton isotopes agree with ORIGEN2 predictions. There were problems with the multiscanning analyzer and these were corrected. Procedures for fission gas sampling (TP-10) and gamma scanning (TP-9) have been updated and approved. The report, "Design and Operations of Systems to Gamma Scan and Fission Gas Sample Spent Fuel Rods Designated as MCC Approved Testing Materials" was submitted for clearance. This report describes fission gas sampling and gamma scanning as well as associated hot cell equipment. C-Ring specimens were prepared from ATM-101 and delivered to the Yucca Mountain Project for testing.

Radiochemical and Solid State Analyses

Radiochemical analysis was conducted for three fuel rods; ATM-103 (moderate burn-up and low fission gas release), ATM-104 (high burn-up and low fission gas release) and ATM-106 (high burn-up and high fission gas release). Ceramography and metallography were conducted on rods from ATM-103, ATM-104, ATM-105 and ATM-106. Grain size and oxide thickness were calculated, and calculations of fuel grain growth were initiated.

Microprobe (EPMA)

Samples 106-NBD107-P and 106-NBD107-Z were analyzed and resulting K ratios reported and the following elements were observed; U, Pu, Cs, Xe, Am, Tc, Nd, Ru and I. Plots of concentration profiles were issued for samples of ATM-103, 104, and 106, and photoimaging of selected elements was conducted. A program, MAGIC IV, is used to convert raw data into wt. percent for the elements examined.

Gap and Grain Boundary Inventory (GGBI)

A document, "Characterization of the Gap and Grain Boundary Inventory (GGBI) in Spent Fuel" was prepared and distributed for review. It contains new techniques which can provide additional data on the GGBI in spent fuel ATMs. Plans for using these techniques were discussed with NNWSI personnel. Methods for quantitatively determining elements in the pellet/cladding gap are being developed. One of these methods involves inductively coupled plasma/mass spectroscopy analysis of the non- and less radioactive

elements dissolved in the acid etch procedure. Particles from the center and outer edge of the rod are being analyzed by shielded scanning Auger electron microscopy.

Data Analysis and Reporting

The report entitled "Characterization of Spent Fuel Testing Material--ATM-106" was cleared and released. The ATM-105 report also has been completed, cleared and released. A paper entitled "Detailed Characterization of the LWR Spent Fuel Rods for the U. S. Repository Testing Program" was presented at the Materials Research Society fall meeting. A paper entitled "LWR Spent Fuel Radiochemical Measurements and Comparisons with ORIGEN2 Predictions" was accepted for publication by the American Nuclear Society. Metallographic, microprobe and autoradiographic data will be presented at the 91st American Ceramic Society meeting in Indianapolis, IN and is entitled "Volatile Fission Product Distributions in LWR Spent Fuel Rods".

Commission of European Communities (CEC) Inter-Laboratory Test

Results were calculated according to CEC protocol and data were recorded on forms provided by the CEC. All tests have been completed, and modifications are being made to adapt the vessels and oven to the flow through system for use in the second half of this round robin. Test materials for the second phase are expected by January, 1989.

D. Support to the Salt Repository Project

Closeout work was completed.

E. Support to the Basalt Waste Isolation Project

Close-out preparations were completed. Equipment eligible for excess was removed. Items not disposed of or redistributed have been reassigned to ongoing projects.

F. Support to the Defense HLW Technology Program

Comprehensive Data Base

This a multi-client task for compiling a data base of properties of nuclear waste glass for use by producers, repository personnel and others involved in the licensing of the storage process. The outline for the data base follows.

- I. INTRODUCTION
- II. SCOPE - MATERIAL COMPOSITION RANGES, etc.
- III. CONVERSION CONSTANTS, SYMBOLS, etc.
- IV. GLASS WASTE FORM PROPERTIES
 - A. LEACHING, DISSOLUTION PERFORMANCE
 - B. THERMAL AND PROCESSING PROPERTIES
- V. MODEL AVAILABILITY FOR WASTE SYSTEM

Data entry of material received from the Catholic University of America (CUA), Savannah River Laboratory (SRL) and the Hanford Waste Vitrification Project was completed.

A three volume draft for comments was distributed to sponsors and others. These volumes included the following.

- Volume 1. 1985 - 1988 Data from Static Glass Durability Tests
- Volume 2. 1979 - 1984 Data from Static Glass Durability Tests
- Volume 3. Glass Durability Flowing Test Data; Data on Thermal and Processing Properties

Comments were received from SRL and DOE-RL, and are being reviewed and necessary changes are being made. WVDP suggested no changes and felt that data base should continue as it is. Work is underway to convert the data spread sheets from the Lotus 1-2-3 format to the Microsoft Excel format. Plans for the future are to provide data in formats suitable for both IBM and Apple/MacIntosh computers.

G. Support to the Savannah River Laboratory

Product Consistency Test (PCT) Round Robin.

Previously, samples were sent to eight participants for the round robin test. Data have been received from the MCC, Corning Glass Works, the University of Florida, Argonne National Laboratory and PNL-MCC and have been entered into a MacroVax data base system. Statistical analysis was conducted to compare the mean and the within laboratory standard deviation, to determine the ability of a given laboratory to discriminate among similar glasses using the product consistency test procedures. Results of this statistical analysis showed that the ability to discriminate depends on short term within laboratory procedural and analytical precision, the number of replicate tests, the number of times each replicate leachate is tested, and the probability of decision errors

(failing to detect a difference of a given size or detecting a nonexistent difference) that are acceptable. Table 1 shows examples of differences from a laboratory with better precision (level A) and a laboratory with less precision (level B). An example for comparing laboratories A and B is that A, with two replicates, can distinguish boron composition differences of 18.1 percent and with three replicates, can distinguish boron differences of 10.1 percent. The less precise laboratory B, with two replicates, can distinguish boron composition of 41.2 percent, etc. A more complete description of the test and the implications of the statistical results are needed.

TABLE 1. Percent Relative Differences in Elemental Releases from Two Glasses That Can be Detected by the PCT (With 95% Confidence and 5% False Alarm Rate)

Level of Lab Performance(a)	n(b)	Element						
		Al	B	Fe	K	Li	Na	Si
A	2	17.9	18.1	63.5	25.9	17.6	14.4	14.6
	3	9.9	10.1	35.2	14.4	9.8	8.0	8.1
	4	7.7	7.8	27.3	11.1	7.6	6.2	6.3
	5	6.5	6.6	23.2	9.5	6.4	5.2	5.3
	7	5.3	5.3	18.6	7.6	5.2	4.2	4.3
	10	4.3	4.3	15.1	6.2	4.2	3.4	3.5
B	2	62.6	41.2	160.6	61.5	53.3	55.5	35.9
	3	34.7	22.8	89.1	34.1	29.6	30.8	19.9
	4	26.9	17.7	69.0	26.4	22.9	23.8	15.4
	5	22.8	15.0	58.6	22.4	19.4	20.2	13.1
	7	18.4	12.1	47.1	18.0	15.6	16.3	10.5
	10	14.9	9.8	38.1	14.6	12.6	13.2	8.5

- (a) "A" denotes a higher level of performance (smaller within-lab precision), while "B" denotes a lower level of performance (larger within-lab precision).
- (b) The value "n" denotes the number of replicate PCT tests performed on each of two glasses.

Analytical results for the four glass samples (NBS SRM 623, ARM-1, SRL202-Good and SRL202-Poor) used in the round robin test also were entered in the data base. The analytical results indicated that the two SRL glasses deviated significantly from their intended compositions. The impact of this deviation on the round robin results is being considered. Calculations indicate that SRL202P is the "worst" glass and that NBS SRM 623 is the "best" glass in terms of chemical durability.

DWPF Canister Impact Testing.

The second set of impact tests on the same canisters (7 meter or 23 ft. drop on the top corner) was conducted in late June. After the second test, canister necks were pushed into the hollow plenum, but visual examination revealed no failure of any of the canisters. Strain circle analysis showed up to 50 percent compressive strain in the neck area with the highest deformation. Tensile strain was more moderate. Dye penetrant tests of welds showed no leakage and helium leak testing showed no leakage above 1×10^{-7} atm-cc/sec. One of the canisters was approximately two degrees more horizontal than it should have been and it bounced. One of the bottom corners appeared to have cracked. Analysis of this corner showed that a filler material, different from the 304 stainless steel, had been added to the bottom of this and all the canisters and machined flat so the canister would stand upright during filling with glass.

Results of dimensional measurements of canisters dropped on the top corner show that the average height decrease of the six canisters was 15.6 cm and the average diameter increase in the most affected area near the shoulder weld was 0.45 cm.

The average canister height decrease in percent was 5.2. Dimensional changes for the canister which bounced were about half of these values with an average canister height decrease of 8.64 which was a 2.88 percent decrease. Canisters in earlier tests which were dropped on the bottom had a height decrease of 2.15 cm or 0.29 percent.

Analytical Laboratory Quality Control Guidelines.

Suggestions received were considered and implemented where appropriate in the document, "QA/QC Guidelines for Analytical Laboratory Practices for Application in the Nuclear Waste Repository Program". A final working draft was distributed to all workshop participants and their management.

H. Support to West Valley Demonstration Project

Reference Glass Chemical Durability Testing.

The PNL report, "Status Report on Pulsed Flow of ATM-10 and WVCM-50" was issued. Pulsed flow test results for boron release from the WVCM-50 (CUA glass) are shown in Figure 1 along with results from reference glasses ATM-10 and AF6 (CTS glass) for comparison. Figure 2 shows leach data for twenty three 28-day partial leachant exchanges for pulsed flow testing of ATM-10. Figure 3 shows results from seventeen 28-day partial leachant exchanges for pulsed flow testing of WVCM-50. Some of the data from the MCC-3 pulsed flow tests are nearly identical with data from the MCC-1 static leach tests for the ATM-10 and the CUA glasses. MCC-1 tests of ATM-10, CUA (WVCM 50) and CTS (SF-6) glass show that the ATM-10 and the CUA glass were more durable than the CTS (SF-6).

Fabrication, Characterization and Leach Testing of a Glass Containing West Valley Waste.

The search for a melting vessel for sludge glass was narrowed to either a high density alumina boat or crucible, or a platinum foil mold liner. Determining factors in the selection were the reaction zone thickness between the alumina and the glass and the degree to which the glass stuck to the platinum. Tests indicated that it would be best to use the alumina container since there was strong adhesion of the melt to the platinum surface.

Difficulties have been encountered in the fabrication of the West Valley sludge glass due to the small amount of starting material. Foaming remains a problem but reducing the amount made at one time could solve this problem.

Experimentation continues on batch development and melting procedures. The sludge should be as similar as possible to ATM-10 and with an $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio sufficient to give a reduced oxidation state.

A copy of the leaching procedure, MCC-TP-18, Leaching Tests by the MCC had a PNL technical review and was prepared for final review and approval. Stainless steel leach containers are to be used but due to a possible problem with the stainless steel altering the redox properties of the leachant, fused silica liners were machined for the stainless steel. There is a leachant loss due to condensation between the fused silica liner and the stainless steel container. This loss for one week of testing was 0.25 percent and was considered insignificant.

Figure 1.

Release of B from
 CTS Glass (SF 8), CUA Glass (WVCM 50), and ATM-10
 Pulsed Flow Test, DIW, 80 C

Figure 2.

Releases from ATM-10
Pulsed Flow Test, DIW, 90 C

B Na Si Th U

○ □ △ ◇ ▼

Releases from WVCN 50 (CUA Glass)
Pulsed Flow Test, DIW, 80 C

Figure 3.

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(See instructions on the reverse)

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10. SUPPLEMENTARY NOTES

11. ABSTRACT (200 words or less)

This report summarizes evaluations by the National Institute of Standards and Technology (NIST) of Department of Energy (DOE) activities on waste packages designed for containment of radioactive high-level nuclear waste (HLW) for the six-month period August 1988 through January 1989. Included are reviews of related materials research and plans, activities for the DOE Materials Characterization Center, information on the Yucca Mountain Project, and other information regarding supporting research and special assistance. NIST comments are given on the Yucca Mountain Consultation Draft Site Characterization Plan (CDSCP) and on the Waste Compliance Plan for the West Valley Demonstration Project (WVDP) High-Level Waste (HLW) Form.

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Localized Corrosion	Copper
Nuclear Waste	Zircaloy
Tuff	Borosilicate Glass
Spent Fuel	Irradiation
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