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UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

December 18, 1990

Dr. Charles Interrante
Materials Engineering Section
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U.S. Nuclear Regulatory Commission
Washington, DC 20555

Dear Dr. Interrante:

Enclosed is the revised draft biannual report for the project "Evaluation and Compilation of DOE Waste Package Test Data," NUREG/CR-4735, Volume 7 (FIN-A4171), as you requested. If you have any questions, please call me.

Sincerely,

Anna C. Fraker

Anna C. Fraker
Metallurgist
Corrosion Group
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Enclosure *on the shelf*

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NUREG/CR-4735
Volume 7

**EVALUATION AND COMPILATION OF DOE
WASTE PACKAGE TEST DATA**

BIANNUAL REPORT

Covering the Period February to July 1989

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February 1989 - July 1989

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"Evaluation and Compilation of DOE Waste Package Test Data:
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"Evaluation and Compilation of DOE Waste Package Test Data:
Biannual Report February, August 1988-January 1989," National
Institute of Standards and Technology, August 1988.

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, February through July, 1989. This includes reviews of related materials research and plans, information on the Yucca Mountain, Nevada disposal site activities, and other information regarding supporting research and special assistance. Outlines for planned interpretative reports on the topics of aqueous corrosion of copper, mechanisms of stress corrosion cracking and internal failure modes of Zircaloy cladding are included in Appendix D. Short discussions are given relating to the publications reviewed and complete reviews and evaluations are included. Included in this report is an overall review of a 1984 report on glass leaching mechanisms, as well as reviews for each of the seven chapters of this report.

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EXECUTIVE SUMMARY

This is the seventh biannual progress report by the National Institute of Standards and Technology (NIST) that gives NIST assessments of some 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 February through July 1989 on DOE reports related to activities of the Yucca Mountain Project (YMP). The report also contains seven reviews published previously, as discussed below. Status reports given here highlight the NIST assessments of DOE activities relating to nuclear waste disposal at Yucca Mountain, NV.

Thirteen reviews of technical reports are included in this report. Ten of these reviews deal with glass. Eight of the reviews of glass are of the Final Report of the Defense High-Level Waste Leaching Mechanisms Program, PNL-5157, compiled by J. E. Mendel of the Materials Characterization Center (MCC) with authors from Catholic University, Pacific Northwest Laboratory, Pennsylvania State University, University of Florida, Rockwell Science Center and Lawrence Livermore National Laboratory. The summary report on PNL-5157, and the review of Chapter 4 are published in this NIST biannual report for the first time. The other reviews of PNL-5157 chapters are included in this biannual report but these reviews have been published previously (see Appendix C). There are some editorial differences in the review format for the seven chapters, but all reviews have been updated to include the conclusions of the chapter author. The reviews of PNL-5157 are in Section 3.2. There is a summary review of all chapters, and there is a separate review for each of seven chapters which have the following topics.

- (1) Mechanism of Defense Waste Glass Corrosion
- (2) Surface Layer in Leached Borosilicate Glass HLW Forms
- (3) Environmental Interactions
- (4) Dissolution of Specific Radionuclides
- (5) Radiation Effects
- (6) Phenomenological Models of Nuclear Waste Glass Leaching
- (7) A Computer Code PROTOCOL for a Numerical Simulation of Glass Dissolution

For each chapter, the NIST has conducted a review to identify the following categories of information: (1) the type of literature, (2) materials used, (3) test conditions, (4) analysis methods, (5) uncertainties in data, (6) deficiencies/limitations in data base, and (7) conclusions. A summary of comments given by NIST reviewers of these chapters, with appropriate recommendations, is presented below in the

order indicated above for the seven sections of the NIST reviews. For more details on any one chapter, see the NIST review of that chapter. Since the publication of this report (PNL-5157), MCC has obtained additional results on various topics and on the effect of composition on the leaching rate of glass. The reader is referred to various MCC reports and to reports from SRI, WVDP, and Vitreous State Laboratory at the Catholic University of America.

The reader also is referred to other work conducted at the Oak Ridge National Laboratory^{1,2} that used Rutherford Back Scattering (RBS) experiments to study the deterioration of the glass. This RBS work showed that the attack of water (or brine) on glass is a discontinuous process. The various impurities or mixed-in elements move to the surface. At the same time the SiO₂-glass structure is weakened, and after periods of less than one day (6-10-14 hours!) this weakened "surface layer" sloughs off into the liquid and a new "virgin" surface is exposed to the liquid.

One other glass report deals with the effects of gamma radiation, and the other glass report is a review of a semiannual report on waste form testing from the Argonne National Laboratory. Included also is a report on microbial corrosion of stainless steel that demonstrated that microbial corrosion can occur under anaerobic conditions and although there were differences in the rate of pitting and other attack based on the type of steel, all steels were susceptible to microbial attack. Another report addresses the ¹⁴C release from spent fuel as determined by analysis of gas from the storage canister and indicates that further measurements are needed and additional time considerations are needed if the release rate complies with 10CFR60. A different report on the aqueous dissolution of bare spent fuel provided data regarding the release rate for various radionuclides, and indicated that data were promising regarding meeting the engineered barrier system release rate requirements for some radionuclides such as ²⁴¹Am, ²³⁸Pu and ²⁴⁰Pu.

During this reporting period, it was decided that information papers would be prepared by the NIST on the three following subjects. Outlines for these interpretive papers are included in Appendix D.

1. Mechanisms of Environmentally Induced Fracture and Their Relevance to HLW Containers in the Tuff Environment.
2. Mechanisms of Localized Aqueous Corrosion of Copper and Its Alloys.
3. Mechanisms of Internal Corrosion of Spent Fuel Rods.

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. A. Fraker, Dr. C. Interrante and Dr. P. B. Adams.

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

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

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

1.0 INTRODUCTION

1.1 Background

This is the seventh 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 disposal.

The Yucca Mountain Project deals with the disposal 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 February through July 1989. Material and activities reported deal only with YMP reports or other material pertinent to disposal of high-level waste at Yucca Mountain.

1.2 Reviews and Evaluations

Reviews are created using guidelines that have been established for reviewers. 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 included in Appendix A (pp. A-1 to A-6).

The reviews and evaluations conducted by the NIST over the period February through July 1989 are found on pages B-3 through B-29 of Appendix B. The reviews of all chapters of PNL-5157 on mechanisms of glass leaching are included as Appendix C. Contributing reviewers for these reviews are acknowledged as a group on the cover page of this report.

The current activities of the DOE-sponsored Materials Characterization Center (MCC), which were reviewed and included in previous NIST biannual reports, are not included here, as review of these activities is no longer part of the NIST program.

1.3 Database Activities

The NIST/NRC database presently contains 1122 entries and it uses a commercially available database management system (DBMS), Advanced Revelation®. The database includes 93 reviews and evaluations at this reporting period. Contained in the review files within the database is information on the source of the document, test conditions, materials, analytical methods, uncertainties in data, deficiencies and limitations, conclusions of the author, abstract of the author, relevance to nuclear waste disposal and comments of the NIST reviewer.

The software program, called DATAOUT was modified to contain all reference holdings. These holdings are divided by records into subfields. This program was used to transfer records to the Center for Nuclear Waste Regulatory Analyses (CNWRA). Also, menu screens were modified, and there was an installation of an index system for faster retrieval of files.

1.4 Related Laboratory Testing

Studies involving laboratory testing at the NIST were continued in three areas. The results of these studies will be reported separately at appropriate stages of the work, and 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 three studies are as follow: (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, and (3) Corrosion Behavior of Zircaloy Nuclear Fuel Cladding. Results of the Zircaloy corrosion studies were prepared and submitted for presentation at the Materials Research Society Meeting in Boston, MA, Nov. 28, 1989. These results show that in synthetic J-13 water representing the water found at Yucca Mountain, Nevada, the Zircaloy has a negligible corrosion rate for the time and conditions of the study. There is some indication of localized corrosion, but this effect could be related to the condition of the Zircaloy or to the specimen mounting. This work is continuing. These results and those from the other laboratory testing will be published upon completion of selected parts of the 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, and vitrification activities.

2.1 Yucca Mountain -- Location and Environment

The lack of characterization data from the Yucca Mountain site continues to be a major deficiency in the information needed for design and modeling of the performance of a waste package for high-level nuclear waste and of any containers used as part of the waste packages. Without this information, studies must rely on data that is assumed to represent the Yucca Mountain tuff environment. Thus, while reading the results of the many Yucca Mountain project studies, it must be kept in mind that these assumptions have not been validated.

The Yucca Mountain site has been storage in previous reports, but the information is included again for the convenience of the reader and to establish the assumed environmental conditions presently being used in studies related to waste package durability. Briefly, the YMP 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^{3,4} [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 oxidic. Initial temperatures resulting from the nuclear waste disposal 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 about 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 may 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 various changes including a shift of the pH into the acidic range. Another potential source of pH change is alternate wetting and drying.

3.0 NIST Activities

Thirteen reviews of technical reports are included in this report. There are two new reviews on waste glass. One review is on microbial corrosion of stainless steel and two other reviews are on the topic of spent fuel and associated radionuclide release. Ten of these reviews deal with glass. Eight of the reviews of glass are of the Final Report of the Defense High-Level Waste Leaching Mechanisms Program, PNL-5157, compiled by J. E. Mendel with authors from Catholic University, Pacific Northwest Laboratory, Pennsylvania State University, University of Florida, Rockwell Science Center and Lawrence Livermore National Laboratory. The summary report on PNL-5157, and the review of Chapter 4 are published in this NIST biannual report for the first time. The other reviews of PNL-5157 chapters are included in this biannual report but these reviews have been published previously (see Appendix C). There are some editorial differences in the review format for the seven chapters, but all reviews have been updated to include the conclusions of the chapter author. The reviews of PNL-5157 are in Section 3.2. There is a summary review of all chapters, and there is an separate review for each of seven chapters which have the following topics.

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The reader also is referred to other work conducted at the Oak Ridge National Laboratory^{1,2} that used Rutherford Back Scattering (RBS) experiments to study the deterioration of the glass. This RBS work showed that the attack of water (or brine) on glass is a discontinuous process. The various impurities or mixed-in elements move to the surface. At the same time the SiO₂-glass structure is weakened, and after periods of less than one day (6-10-14 hours!) this weakened "surface layer" sloughs off into the liquid and a new "virgin" surface is exposed to the liquid.

3.1 Reviews and Summaries

Technical reviews completed during the reporting period are presented in Appendices B and C. All reviews presented there have been approved by the NIST Washington Editorial Review Board (WERB).

3.1.1 Waste Glass

Bates: 1988

A more recent update of the Abrajano study is described by Bates in a semiannual report which includes dissolution data for SRL 165 glass up to 104 weeks, and also describes data not reported before on the dissolution of West Valley Glass (ATM-10) during 26 weeks of exposure. Gamma radiation levels used are reported to be 1×10^3 and 0 Rd/h. Radionuclide dissolution measurements are also made in the presence of sensitized Type 304L stainless steel that show an increase in dissolution rate of both stainless steel and radionuclides compared to similar measurements in the presence of non-sensitized stainless steel. This study provides valuable information for high-level-waste licensing.

3.1.2 Stainless Steel

Ringas: 1988

This work demonstrates that microbial corrosion can occur on stainless steels under anaerobic conditions. Though the environment of the tuff repository is expected to be aerobic, under some conditions, in crevices or under debris, anaerobic conditions can develop on the waste containers. Coupons of several stainless steels were totally immersed in deaerated, sterilized culture media over a four month period. Half of the flasks were inoculated with sulfate reducing bacteria and half were left in a sterile media. The results are shown by ranking the alloys in order of decreasing pit density as follows: Sandvik 1802 > mild steel > AISI 409 SS > 3CR12A > AISI 430 SS > 3CR12 > AISI 304L SS > AISI 316L SS >

AISI 316 SS. In general, the higher alloy stainless steels were more resistant to pitting attack, but none were totally resistant to bacterial corrosion.

3.1.3 Spent Fuel

Van Konynenburg: 1984

The generation of gaseous radioactive species in the nuclear waste repository is of concern because the rate of transport for these gases is expected to be high, increasing the danger of contamination of the atmosphere. This study was directed at measuring the rate of generation of ^{14}CO , $^{14}\text{CO}_2$, and $^{14}\text{CH}_4$ from spent fuel rods in an air-filled stainless steel canister at an initial temperature at 275°C over a period of over six months. The data indicate that CO_2 was rapidly produced during the initial stages of the experiment, and at some point in the experiment, a fuel rod breach occurred, releasing an additional amount of CO_2 . Initial interpretation of the data indicates that the release rate will be below the limits given in 40CFR191, but it is questionable whether it will meet the release rate limits set by 10CFR60. Other metals in the canister and the canister itself will contribute nitrogen which may be converted to C when irradiated. UCRL-94708 (described in NUREG/CR-4735, Vol. 5) is a more recent report on the subject.

Wilson: 1987

The release of some radionuclides is particularly significant due to their toxicity and long half-life. This report describes results of dissolution measurements made on uncladded spent fuel in J-13 water at 25°C and 85°C . An unsealed fused silica vessel (Series 2) was used in one case and a sealed type 304L stainless steel container (Series 3) was used in another. Plutonium and americium are the most significant radionuclides with both making up more than 95% of the total Curie activity. The results show that as the six month exposure cycle passed, the rate of dissolution for these radionuclides decreased. High concentrations of carbon-14, as CO_2 , were measured initially in the sealed stainless steel container, but similar measurements could not be made in the unsealed silica since the CO_2 was lost to the atmosphere. In all cases, concentrations of radionuclides were below the maximum allowable release requirements.

3.2 Reviews of PNL-5157 on HLW Leaching Mechanisms

The complete set of reviews of this document is included in Appendix C. A discussion of the reviews and the document was given in the Section on NIST Activities, 3.0.

3.2.1 Overview and Further Interpretation of all the Chapters

Mendel: 1984

This review is a summary of information contained in each of the seven reviews of PNL-5157. The program was administered by Pacific Northwest Laboratories (PNL). This program was set up to determine the dominant leaching mechanisms for defense waste glass and to evaluate the effects of some major

Abrajano: 1988

Using J-13 groundwater at 90°C, in the presence of gamma radiation (1×10^4 rd/h), leaching rates of several radionuclides from Savannah River Laboratory 165 type glass (SRL 165) were determined for times up to 7 weeks. The solution pH decreased during the first 56 to 91 days, and after that steadily increased. The authors believe that this effect was the result of the interaction of nitric acid (radiolysis of N_2) and CO_2 formed in the solution. However, this observed variation in pH had little effect on the dissolution of the actinides. In fact, the dissolution rate in all cases decreased with time.

3.2.2 Review of Chapter 4

Mendel: 1984

Chapter 4, of PNL-5157 is entitled Dissolution of Specific Radionuclides, and the experimental results of the dissolution of technetium, uranium and transuranic elements from glass. Glasses studied included the borosilicate type, defense waste reference glass (DWRG) doped with radionuclides and iron and MCC 76068 glass. These radionuclides, due to their long half lives, are of significance to the long-term safety of the nuclear waste repository. Dissolution of these radionuclides is affected by the Eh (oxidation potential) of the solution. Dissolution of technetium, in particular, is slowed by reducing conditions. Thermodynamics, measurement and control of Eh are discussed. The presence of iron was another factor that enhanced the overall leaching rate. The mechanism for this enhancement by the presence of iron was explained based on the oxidation of the iron to produce ferrous ions that in turn reacted with dissolved silica to form a precipitate with the end result being a solution undersaturated with silica, and this increased the driving force for further dissolution of the glass.

4.0 References

1. Sales, B. C., White, C. W., and Boatner, L. A., "Application of Ion Implantation and Backscattering Techniques to the Analysis of Nuclear Waste Glass Corrosion," Mater. Lett. (Netherlands), Vol. 2(1), 1-5, 1983.
2. Sales, B. C., Begun, G. M., White, C. W., Boatner, L. A., Green, P. H., and Watson, D. M. (Eds.), "Surface Layer Formation on Corroded Nuclear Waste Glasses, Oak Ridge Nat. Lab. Report No. ORNL-6128, 213-214, March 1985.
3. Soo, P. and Gauss, E., "Review of DOE Waste Package Program," NUREG/CR-2482, Vol. 7, 1985.
4. McCright, R. D., Halsey, W. G., and Van Konynenburg, R. A., "Progress Report on the Results of Testing Advanced Conceptual Design Metal Barrier Materials Under Relevant Environmental Conditions for a Tuff Repository," UCID-21044, December 1987.

**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 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

| Waste Glass | Page |
|---|------|
| Abrajano, T. A., Bates, J. K., Gerding, T. J., and Ebert, W. L., ANL-88-14 "The Reaction of Glass During Gamma Irradiation in a Tuff Environment" | B-3 |
| Bates, K. K., Gerding, T. J., Gbert, W. J., Mazer, J. J., and Biwer, B. M., UCRL-21060-87-2 "NNWSI Waste Form Testing at ANL," Semiannual Report | B-12 |
| Stainless Steel | |
| Ringas, C. and Robinson, F. P. A. "Corrosion of Stainless Steel by Sulfate- Reducing Bacteria--Total Immersion Test Result" | B-18 |
| Spent Fuel | |
| Van Konynenburg, R. A., Smith, C. F., Culham, H. W., and Otto, C. H., Jr., UCRL-90855 "Behavior of Carbon-14 in Waste Packages for Spent Fuel in a Repository in Tuff" | B-21 |
| Wilson, C. N., UCRL-21013 "Summary of Results from the Series 2 and Series 3 NNWSI Bare Fuel Dissolution Tests" | B-25 |

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Argonne National Laboratory, Argonne, Illinois

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

Abrajano, T. A., Bates, J. K., Gerding, T. J., and Ebert, W. L.

"The Reaction of Glass During Gamma Irradiation in a Tuff Environment"

ANL-88-14, February 1988

DATE REVIEWED: 7/22/89

PURPOSE

The experiments were performed as part of an effort by the Nevada Nuclear Waste Storage Investigations Project to assess the importance of radiation effects on repository performance and waste glass corrosion. The gamma radiation field used in this work was $1.0 \pm 0.2 \times 10^4$ rd/h.

"Savannah River Laboratory 165 type glass was leached with equilibrated J-13 groundwater at 90°C for times up to 182 days." "To understand the effect of radiation on groundwater chemistry and waste form durability, NNWSI is performing an extensive set of radiation experiments as a function of dose rate (2×10^5 , 1×10^4 , 1×10^3 , and 0 rd/h." "This report presents the results of the tests done at 1×10^4 rd/h and discusses the relevance of these tests to repository conditions."

KEY WORDS

Experimental data, leaching, microscopy (light, electron, SEM, etc.), spectroscopy, surface film, laboratory, J-13 water steam, J-13 water, Cu, Fe, tuff, alpha radiation field, gamma radiation field, ambient pressure, ambient temperature, basic (alkaline) solution (ph >7), static (no flow), stainless steel, 304L stainless steel, welded, glass (defense waste reference glass), defense high-level waste (DHLW), ^{137}Cs , Sr, ^{237}Np , ^{238}Pu , ^{241}Am , J-13 steam, J-13 water, tuff, leaching (radiation enhancement).

CONTENTS

This 124-page report consists of an abstract, an executive summary, an introduction, a summary and conclusions, an acknowledgement, 30 figures, 12 tables, and the following content:

| CONTENT | PAGES |
|-------------------------|-------|
| Experimental | 10 |
| Results | 48 |
| Discussion | 37 |
| Appendix I, II, III, IV | 10 |
| References (35) | 4 |

TEST CONDITIONS

Materials:

- glass: SRL U (SRL 165 black frit to which uranium, cesium, and strontium had been added).
SRL A (SRL U glass to which ^{237}Np , ^{239}Pu , and ^{241}Am had been added.)
- vessel: Type 304L stainless steel.
- rock: (1) tuff from USW-G1, 1235.1-ft. and 1232.2-ft. levels.
(2) tuff supplied by NNWSI (UE-25h #1, 173.0-ft to 173.6-ft. levels).
(3) tuff from USW-62, 1235.1-1232.2 ft.-level.

Specimen Preparation:

- glass: One of the two disks used in each test had one side ground to 600 grit. Therefore, three different types of glass surfaces were present in each test; both faces of one disk and the bottom side of the other disk are as cut, the top side of the other disk is ground to 600 grit, and the sides of the disks are as cored. The glass surface area to solution volume ratio was nominally set at 0.3 cm^{-1} .
- rock: polished tuff core wafer.

Environment: EJ-13, EJ-13 plus tuff, EJ-13 vapor and EJ-13 vapor plus tuff at a nominal temperature of 90°C and at a gamma-dose rate of $1.0 \times 10^4 \text{ rd/h}$ (total dose up to $4.4 \times 10^7 \text{ rads}$) for 14 to 182 days. The vessels have a capacity of 21.4 cm^3 and were sealed with a compression fitting and a silicon rubber gasket.

UNCERTAINTIES

- gamma dose rate : $\pm 0.2 \times 10^4$ rd/h.
- temperature : $\pm 0.5^\circ\text{C}$.
- selected activities in SRL A glasses : SD (standard deviation) from 0.031 to 27.77 (% SD from 8.98% to 26%).
- "1 σ " (not specified, we assume this to be one of SD definition from the probabilities distribution function).
"Variation of Np and Am between glass disks were within 20 and 10 percent of their mean, respectively. The experimentally determined analytical precision of the 2-counting facility was less than 10%."
- "Water loss for experiments performed for less than 182 days did not exceed 0.10 g, whereas the maximum water loss noted for the 182-day experiment was 0.25 g."
- "A 2-KeV neon ion beam was used for SIMS. The sampled area is of the order of 1 mm²."
- Analytical accuracy and precision from repeated analyses: "3-10% (cation), 5% (anion), 5% (uranium), 10% (dissolved gases), and 0.02 unit (pH)."
- Experimental accuracy and precision: "Because of statistical limitations, several sources of error are identified."
 - "compositional inhomogeneity of glass and tuff"
 - "the contamination of the solution with Si from the gasket material"
 - "the contamination of the solution after termination of the run. A speculative scenario is that refluxing gases vaporized during the 90°C acidification could have condensed on some portions of the Si gasket, reacted with the gasket and dripped back to the solution."
- "opted to present results of duplicate experiments to give the reader a better feel for the experimental uncertainties, rather than the overall precision (i.e., experimental and analytical) to be $\pm 7\%$ for Na, $\pm 4\%$ for B, $\pm 5\%$ for all anions, $\pm 15\%$ for the actinides and $\pm 10\%$ for all other cations, which were estimated in the previous report."
- "the overall variations in the concentrations of anions (F⁻, Cl⁻, NO₂⁻, NO₃⁻ and SO₄⁻²) are only between 10 to 20 percent (1 σ) of their mean values for the EJ-13 only experiments." "Greater variations were observed in the concentrations of NO₂⁻ and NO₃⁻ for the EJ-13+ tuff experiments, but even these are within 30% of their mean abundances in all the tests."
- There are cross-hatched regions in figures showing the uncertainties: time vs pH, NO₃⁻/NO₂⁻ vs pH.
- There was an "analytical artifact in Nuclear Resonance Profiles arising from the presence of irregular morphology on the reacted glass surfaces."

- In SIMS analyses, "sputtering depths measured using both methods 2 and 3 agree within 10%" (method 2 : by surface profilometry (Dektac) of glasses sputtered for known periods of time; method 3 : by sputtering layers of known thickness as measured by SEM).

DEFICIENCIES/LIMITATIONS IN DATABASE

- "Some comments on the relevance of the results to actual repository scenarios are" "not intended to be exhaustive, as there are certain experimental parameters that have been of standard use in NNWSI repository-oriented tests which are more elaborately discussed elsewhere, e.g., NNWSI Site Characterization Plan." Such parameters are temperature, glass composition, EJ-13 solution, radiation levels and dose rate, H₂O liquid volume, various configuration of glass associated with tuff, homogeneity of host rocks, pressures of gas phase and water steam, the ratio of gas volume to liquid volume, pH drift, availability of buffering species such as HCO₃⁻, and the ratio of glass surface area to solution volume. "A thorough analysis of even some of the experimental parameters adapted in the present program may be premature because more experiments are in progress in our laboratory to further understand the interactions which occur in the reaction vessels and to refine the experimental methodologies." "Several experiments designed to further understand NNWSI repository conditions after waste package emplacement are actively being pursued in other laboratories, foremost of which is LLNL."
- "The gamma dose rate used in the present work is higher than the dose rates appropriate for a SRL glass canister breached sometime during the containment period." "Accelerating the effect of γ -radiolysis by increasing the dose rate without accelerating other interactions (e.g., waste glass corrosion) can unduly influence the glass corrosion mechanism and elemental release pattern, e.g., actinides."
- "The Si concentration in solution is going to be higher in systems with high SA/V ratio compared with systems with low SA/V ratio." "Practically, there is no evidence that the leachate is independent of SA/V ratio."
- "(SA/V . t) scaling can be used to predict long-term release rates only if fractional leach rates are a function of solution concentration only."

CONCLUSIONS OF AUTHOR

The measured pH's in both the blank and actual runs followed a trend of decreasing values to 56 or 91 days and increasing values after 91 days. We attribute this variation to the interplay between acidification by nitric acid production (radiolysis of N_2) and basification by $CO_2(g)$ loss from solution. In the presence of SRL glass, exchange reactions between the hydronium ions or protons from solution and mobile cations (e.g., Li and Na) from the glass further basified the solution. However, the overall effect of glass corrosion on solution pH in the present experiments is not dramatic, and a narrow pH range of 6.7 to 7.5 prevailed for the whole duration of the experiments.

The only significant anion variation observed in the leaching experiments is the systematically lower NO_3^-/NO_2^- ratios from EJ-13 only to EJ-13 + tuff to EJ-13 + tuff + glass experiments. This observation could be attributed to the catalytic effect of reduced species on silicate surfaces upon radiolytic reactions that ultimately lead to nitrate breakdown [VON KONYNENBURG].

The general normalized release pattern, $Li \geq Na \geq B \geq Si$, was exhibited by the solution data. A single parabolic function could be fitted to Li and Na (to 91 days) regardless of the presence or absence of tuff. The release rate of B and Si also slowed down with time.

The nuclear resonance profiles for H and the SIMS profiles for Li, Na, B, Al, Ca, Mg, Mn, and Fe indicated two regions in the reacted layer. The region closer to the unreacted glass, referred to as the transition zone, exhibits well-defined S-shaped profiles for H, Li, Na, and B indicative of concentration-dependent diffusion coefficients for these elements during interdiffusion. The region away from the glass, referred to as the gel layer, exhibits relatively flat profiles for these elements.

Speculations on the mechanisms of release of individual glass species were based on the above information. Lithium, and Na are released from the glass via ion-exchange (with proton or hydronium) across the transition zone while B diffuses from the transition zone after pathways for diffusion are established. The transition zone behaves as a transport barrier to these species. On the other hand, the dominant mode of Si release is etching of the gel layer. Some Si may be released from within the gel layer as speculated by [GRAMBOW], but this amount is probably a minor contribution to the overall Si-release. Transport of H, Li, Na, and B across the gel layer is rapid compared with diffusion across the transition zone.

The depth profiles showed that the transition zone grew at a decreasing rate with time, a finding which agrees with the leachate data. Approximate calculations of the rates of gelation and etching suggest that both rates also decrease with time. We attribute these decreased rates with time to saturation effects.

The release of other major glass species were considered within the framework of the mechanism discussed above. The variation of the normalized solution concentrations of Mg and Sr with time is consistent with their release via etching. A similar release mechanism may explain the release pattern of Ca, but some influence of secondary phase precipitation is also indicated. The SIMS profile for Ca and Fe shows an enrichment in the gel layer. Early precipitation of Al phase(s) is indicated by the solution data.

The actinide elements, Pu and Am showed total normalized release patterns that are approximately linear with time to at least 91 days. We tentatively ascribe this release pattern to a combination of matrix breakdown and reconstitution in the gel layer, although preliminary ion microprobe profiles suggest that Pu and Np behavior may be more complex. The significant correlation between pH with Pu, Np, and Am concentrations in unfiltered nonacidified samples suggests that solubility is the key parameter controlling their concentration levels in solution.

The presence of tuff did not appear to affect the mechanism of release of the major glass species. Because tuff also dissolved in solution, a faster approach to saturation of secondary products was noted where tuff was present. The present data strongly indicate that some sorption of actinides to the tuff surface has occurred. Larger total actinide release was noted in the case of Pu and Am in tuff-containing experiments. This observation is attributed to the lower integrated pH values attained in the tuff-containing experiments in the present program.

Some preliminary comments were made on the applicability and limitations of the present results to predicting the nature of actual interactions in the NNWSI repository. Specific attention was given to test configuration, test component materials, R, γ -dose rate, and SA/V ratio. The present results, together with those of the previous [BATES-1] and ongoing experiments, will be evaluated in the future to provide more definitive assessment of the repository relevance of these experiments.

RELATED REPORTS

1. Bates, J. K., Fischer, D. F., and Gerding, T. J., "The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part I: SRL 165," ANL-85-62 (1986).
2. Bates, J. K., Ebert, W. L., Abrajano, T. A., Mazer, J. M., and Gerding, T. J., "NNWSI Waste Form Testing at Argonne National Laboratory," Semiannual Reports for July-December 1985 until Present, UCRL-1580, in press.
3. Bates, J. K. and Gerding, T. J., "One Year Results of the NNWSI Unsaturated Test Procedure: SRL 165 Glass Application," ANL-85-41 (1986).

COMMENTS OF REVIEWER

1. This report presents unique data of radioactive glasses leaching which cannot be obtained easily in many other laboratories. Therefore, the data presented here are very valuable for HLW licensing applications.
2. The authors provide the readers with their elaborate analysis of the experimental errors. They could easily identify the analytical errors. However, the experimental errors have been concluded to be very difficult to be assessed, leaving them for a future task. The reviewers recommend an adoption of statistical theories in such difficult circumstances. An example of those theories is the extreme value theory.
3. Much longer tests, or valid accelerated tests, are recommended to be performed. The main reason for this recommendation is the incongruency of leach rates accompanied by pH drift or by the diffusional movement of the altered surface layer, which makes it difficult to predict the long-term performance of waste glasses.
4. The authors point out that colloid formation has not been analyzed at this point. Considering the portion of the dissolved species in acidified solutions is substantial, this topic should be explored further. Likewise, the sorpted elements on host rocks or stainless steel should be reanalyzed in this regard too.
5. The purpose of surface analysis was very clearly stated in this report (p. 74), which is very unusual among so many works in the surface analysis of waste glasses. The reviewers further recommend that attempts be made to tailor glass compositions minimizing the leach rates based on these surface analyses.

6. While the generic leaching behavior of generic elements has been analyzed very extensively, their correlation with the analyses to radioactive elements is quite limited. The recommendation is that this be explored further for the licensing applications.

7. In many instances, the authors use solubility limits in analyzing leach data. We should be cautious about using the solubility limits because they are of thermodynamic equilibrium concepts. When precipitates are growing, those solution concentrations can be dynamically balanced ones. For instance, on page 91, actinides release rates was attributed to the pH dependence of the actinides solubilities. This can be explained by the pH dependence of reaction constants when viewed as the kinetic processes.

8. More elaborate efforts in cross-comparison of various data are necessary in interpreting data using multiple variables, rather than simple speculations using data from one variable. An example is the long-term decrease of leach rates. This behavior should be explored further by analyzing their dependence on other variables such as colloid formation, pH change, Eh change or altogether.

9. If the authors like to interpret their data in terms of solubilities, they are recommended to estimate the redox conditions more quantitatively. The importance of Eh condition in leaching has been well recognized in many related papers in glass leaching.

10. There have been minor errors found by the reviewers, which, in some cases, could be important.

- On p. 68, the corrosion of stainless steel can be a source of proton generation too by the oxide formation with water molecules.
- On p. 70, the low O₂ and N₂ concentrations have been attributed to air leakage. If they are in equilibrium with air, there would be no leakage.
- The fitting experimental data to $t^{1/2}$ or t should be reconsidered. In many such formulations in chemical kinetics, there are constant terms involved, which change the curve behavior significantly.
- On p. 78, there were assumptions of using zeroth- or first-order kinetics. Some examples of such order kinetics from generic kinetics seem to be necessary to justify these assumptions.

- On p. 97, it is stated that "NNWSI site will not be saturated" these will be areas of local saturation (e.g., ring around waste package. Also, some areas of repository may be saturated for long periods. To justify the present work in aqueous environments, this scenario should be re-reviewed, or at least a worst case scenario should be presented.
- On p. 11 and p. 33, there appear to be typographic errors: total dose 5×10^8 rad not rd/h, and $V_f^{-1}(S_A)^{-1}$ should be $V_f(S_A)^{-1}$ or $V_f^{-1}(S_A)$.

APPLICABILITY OF DATA TO LICENSING

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

- (a) Relationship to Waste Package Performance Issues Already Identified
 - 2.3.2 regarding the solubility of the waste form under potential repository conditions
 - 2.3.2.1.2 regarding rates of dissolution
- (b) New Licensing Issues
 - Effects of gamma radiation on waste form dissolution.
- (c) Comments related to Licensing

ABSTRACT

Savannah River Laboratory 165 type glass was leached with equilibrated J-13 groundwater at 90°C for times up to 182 days. These experiments were performed as part of an effort by the Nevada Nuclear Waste Storage Investigations Project to assess the importance of radiation effects on repository performance and waste glass corrosion. The gamma radiation field used in this work was $1.0 \pm 0.2 \times 10^4$ rd/h.

Glass dissolution is notably incongruent throughout the entire experimental periods and normalized releases follow the sequence $Li \geq Na \geq B \approx U \geq Si$. The normalized leach rates of these elements, as well as the measured growth rates of the reaction layers, decreased with time. The only significant variation observed in the abundance of anions is the systematic decrease in NO_3^-/NO_2^- ratio from the starting EJ-13 groundwater to the EJ-13 blank experiments to the tuff- and glass-containing experiments. A leaching model that is consistent with the observed solution data and depth profiles is presented. The applicability and limitation of the present results in predicting the actual interactions that may occur in the NNWSI repository are discussed.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA.
For the NNWSI Project, U.S. DOE.

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

Bates, J. K., Gerding, T. J., Gbert, W. L., Mazer, J. J.,
and Biwer, B. M.,
"NNWSI Waste Form Testing at ANL," Semiannual Report
UCRL-21060-87-2, July 1988.

DATE REVIEWED: 7/1/89

PURPOSE

Overall:

"To study the behavior of waste form under anticipated repository conditions. These experiments include (1) the development and performance of a test to measure waste form behavior in unsaturated conditions, (2) the performance of experiments designed to study the behavior of waste package components in an irradiated environment, and (3) the performance of experiments to investigate the reaction of glass with water. Previous reports document developments in these areas through June 1987. This report summarizes progress during the period July-December 1987."

Specific Test:

- "The unsaturated test method has been developed to study materials interactions (water/waste form/metal/air) that may occur in an unsaturated environment and to provide a measure of radionuclide release from a waste package assemblage (WPA) consisting of the waste form and metal components of the waste package."

- "The purpose of the characterization of the interacted components of the batch tests with SEM/EDS and XRD is to (1) provide a description of the reaction progress independently of the solution results; and (2) catalog and identify alteration products that form during the course of the reaction."

- "There are several purposes of the parametric experiments. They are to study (1) the effect of waste form surface area, (2) the effect of water drop size, (3) the effect of lengthening the time interval, (4) the release of U from non-reacted fuel pellets, (5) reaction product presentation, (6) the effect of pre-sensitizing stainless steel (SS) holder, (7) the effect of water saturation on glass reaction, (8) the use of vapor phase hydration and natural analogs, (9) the effect of time and temperature on the hydration, and (10) the verification of the effect of sensitization on glass reaction."

- "The relative humidity experiments were designed to (1) probe the dependence of hydration on humidity, (2) test the effect of different glass compositions on (1), and (3) compare the hydration products formed on the various glasses."

- "A series of hydrothermal leaching and vapor phase hydration experiments have been performed using two synthetic basalt and one SRL glass composition and deionized water." "While these experiments were completed under a different sponsor, they provide a wealth of samples and data that still require analysis and interpretation, where the synthesized information will be of use to the NNWSI program. For this reason work is continuing with these samples."

- "The purpose of the preliminary experiment of the vapor reaction method is to gain an appreciation for the rate at which these glasses react under various conditions in order to generate a reaction matrix scheme which will properly monitor the reaction progress."

KEYWORDS

Experimental data, leaching, microscopy (light, electron, SEM, etc.), spectroscopy, surface film, x-ray diffraction, laboratory, Yucca Mountain, air, J-13 water, deionized, tuff, gamma radiation field, acidic solution (ph >7), ambient pressure, ambient temperature, dynamic, high pressure, high temperature, static (no flow), stainless steel, zircaloy, sensitized, glass (West Valley reference glass), glass (defense waste reference glass), obsidian, basalt, UO₂ pellet, PNL-76-68, commercial high-level waste (CHLW), defense high-level waste (DHLW), spent fuel, Np, Pu, Am, U, (isotope numbers not stated), J-13 steam, J-13 water, DIW, tuff, dissolution, leaching (radiation enhancement), leaching (spent fuel).

CONTENTS

This 98-page report consists of an abstract, 34 figures, 20 tables and the following content:

| CONTENT | NUMBER OF PAGES |
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| NNWSI Waste Form Testing | 17 |
| NNWSI Parametric Experiments | 7 |
| Relative Humidity and Simple Glass Experiments | 28 |
| Gamma Irradiation Experiments | 7 |
| Analytical Support | 4 |
| Basalt Analog | 16 |
| NNWSI Vapor Hydration Experiments | 17 |
| References (23) | 2 |

TEST CONDITIONS

Materials:

- Waste Package Assembly (WPA) consisting of the waste form and metal components
- 304L ss and tuff rock
- Glass - simple glass, ATM-10, ATM-10-2, ATM-1C/8, ATM-1C, ATM-8, Basalt, obsidian, SRL-131, PNL 76-68, SRL-165, SRL-165 U/A, SRL 165U, WV U/A, SRL Black Frit, WV 50, WV 44
- UO₂ Pellets encased in Zircaloy cladding

- Specimen preparation:
- polished
 - as-cut
 - powdered
 - crushed
 - disk

- Environment:
- unsaturated test method dripping water periodically on the WPA or vapor test at (RH) of 60, 95, and 100% and at 753°C
 - Batch tests and continuous flow tests (conditions stated in previous reports)
 - MCC-1 leach test in J-13 well water or DIW at 903°C
 - Radiation - 2E5, 2E4, 2E3 and 0 R/h gamma radiation at 903C in J-13
 - Hydrothermal test in DIW at 90°C-187°C and at 122-240°C, and in vapor at 188°C.

UNCERTAINTIES IN DATA

- Composition of Hawaiian Basalt: ±0.01 to ±0.13 STD.
- Reaction Layer chemistry of SRL 165 and Basaltic glasses from hydrothermal tests at various testing temperatures: ±0.01 to ±2.52 weight percent.
- Reaction Layer thickness of Hawaiian Basalt leached in DI water at 187°C at various time: error bar approximately up to 55%.
- Reaction Layer thickness of SRL frit in saturated DI water vapor at 187°C: error bar approximately as high as 90%.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

There is no statement of overall conclusions in this report except the conclusion of subsection I.A.2 concerning N2 unsaturated test. The ABSTRACT contains the essence of the work performed in this particular period.

I.A.2 N2 unsaturated test

A complete discussion of the above results is presented on the unsaturated condition. The conclusions drawn from the work are that the N2 Unsaturated Test series, which are specific to the NNWSI repository site, result in the formation of several identifiable reaction phases and reasonably constant elemental concentrations in solution. The next step in interpreting the reaction process will be to use geochemical modeling codes in conjunction with the solution and phase results reported here to see if any correlation between the modeling theory and the results exists.

Other data presented suggest that when sensitized 304L stainless steel (SS) in contact with glass is also contacted by small volumes of repository water, a reaction occurs resulting in the formation of metal (Fe, Cr, Mn, Ni) silicate phases. This reaction accelerates the breakdown of the 304L SS and the reacted glass surface, thereby increasing elemental release up to ten times the amount observed with non-sensitized SS. However, the glass breakdown does not necessarily result in equal release to solution of all the actinide elements. Neptunium is released to solution without significant fixation in alteration phases or adsorption on metal components. However, U forms stable crystalline phases which decreases its concentration to solution. The release of Pu and Am to solution is even more greatly reduced as these elements strongly adsorb to the reaction products and the metal surfaces.

The tests reported here are still in progress and will be continued to gain additional information regarding glass/metal/water interactions under unsaturated conditions.

RELATED REPORTS

1. M. J. Steindler, et al., "Quarterly Progress Report, Nuclear Fuel Cycle Section," Argonne National Laboratory Topical Reports, ANL-8437, ANL-84-57, and ANL-84-91 (1984).

2. J. K. Bates, et al., "NNWSI Waste Form Testing, Semiannual Report, July-December 1985," Lawrence Livermore National Laboratory, UCRL-1580 (1986).
3. J. K. Bates, et al., "NNWSI Waste Form Testing, Semiannual Report, January-June 1986," Lawrence Livermore National Laboratory, in press.
4. J. K. Bates, et al., "NNWSI Waste Form Testing, Semiannual Report, July-December 1986," Lawrence Livermore National Laboratory, in press.
5. J. K. Bates, et al., "NNWSI Waste Form Testing, Semiannual Report, January-June 1987," Lawrence Livermore National Laboratory, in preparation.
6. J. K. Bates and T. J. Gerding, "Application of the NNWSI Unsaturated Test Method to Actinide Doped SRL Type Glass," Argonne National Laboratory, in press.
7. J. K. Bates and T. J. Gerding, "The Performance of Actinide-Containing SRL 165 Type Glass in Unsaturated Conditions," presented at the Symposium for the Scientific Basis for Nuclear Waste Management, Materials Research Society Meeting, December 1-4, 1987. Boston, MA.
8. J. K. Bates, D. F. Fischer, and T. J. Gerding, "The Reaction of Glass in a Gamma Irradiated Saturated Tuff Environment, Part 1: SRL 165 Glass," Argonne National Laboratory Topical Report, ANL-85-62 (1986).

COMMENTS OF REVIEWER

1. This work has selected pertinent experimental variables quite effectively in dealing with the complicated system of glass leaching under various environmental conditions. Particularly, the studies of synergetic effects among components of the waste packages provide key information.
2. The reviewers have difficulties in understanding the categories of the report. It is recommended that, (1) the relative comparison of various test methods tested, and (2) the relative comparison of the results from various materials be summarized to obtain a comprehensive understanding.
3. A significant portion of the work has been in the surface analysis for the determination of the chemistry and thickness of alteration-layer. However, it is not clear how this will be interpreted in terms of long-term leach rates of radionuclides for regulatory purposes. Examples

may be (1) that this study will lead to a very low leach rate glass by forming an inert alteration layer or (2) that the alteration layer will be equilibrated with the solution and subsequently will determine the leachate chemistry.

4. In interpreting the leach data under gamma irradiation, it may be necessary to consider the basicity produced during leaching itself in addition to radiolysis effects which are reported to cause leachate acidification.
5. In the humidity tests, the authors need to clarify whether the humidity tests are to understand what happened to partially wetted glass or the glass in moist atmospheres. By the time the container fails, the glass is very likely to be in solution, at least partially.

APPLICABILITY OF DATA TO LICENSING

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

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

2.3.2 What is the solubility of the waste form under the range of potential repository conditions?

- (b) New Licensing Issues
- (c) Comments Related to Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Dept. of Metallurgy, Univ. of Witwatersrand, 1 Jan Smuts Ave., Johannesburg, 2001 South Africa

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

Ringas, C. and Robinson, F. P. A.
"Corrosion of Stainless Steel by Sulfate-Reducing Bacteria--Total Immersion Test Result,"
Corrosion Engineering, 44, (9), 671-678, 1988.

DATE REVIEWED: 6/9/89

PURPOSE

Tests were conducted over a four month period to "unequivocally show that sulfate reducing bacteria (SRB) could cause corrosion of stainless steels".

KEY WORDS

Corrosion, mild steel, 304 stainless steel, 316L stainless steel, microscopy, weight change, laboratory, bacteria culture medium, microbial corrosion.

CONTENT

There are nine pages of text and figures, and six references are given. There are twenty four figures showing the test vessel and scanning electron micrographs of mild steel and several stainless steel surfaces after various stages of corrosion by SRB. There are two tables. One table shows the weight loss for all of the alloys studied after exposure to specific bacteria strains. The other table shows pit density counts for the various specimens.

AMOUNT OF DATA

There are 26 figures (micrographs) and 2 tables.

TEST CONDITIONS

Specimens which had been ground through 120 SiC grit paper were washed and passivated in 40% HNO₃ for one h before testing. Other specimens for crevice corrosion tests were clamped together with rubber bands between two teflon washers.

Specimens were sterilized in an autoclave at 120°C for 15 min prior to being placed in four two liter flasks. Three of the flasks contained bacterial cultures and the fourth was sterile growth medium that was used as the control. Specimens were observed only at the end of the test and special care was taken for necessary medium additions to avoid contamination. Specimens were removed at the end of the test, cleaned with a nylon brush and distilled water, weighed and then observed in the stereomicroscope at 15X and in the scanning electron microscope (SEM). Specimens included 3CR12, 3CR12A, 3CR12B, AISI 409, AISI 430, Sandvik 1802, AISI 304L, AISI 316L, AISI 316, Mild Steel. Strains of SRB were 8303, 8312 and a mixed strain.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF THE AUTHOR

"These total immersion tests results show that stainless alloys are susceptible to microbial corrosion.

The actual mechanism of corrosion is complex and includes the establishing of differential aeration cells and the generation of sulfur species such as H₂S.

... all the alloys suffered higher weight losses in the bacterial cultures than in sterile medium because of the metabolic end products of the bacteria.

The resultant corrosion manifested itself in two forms, namely intergranular corrosion and pitting.

A distinctive shiny surface was produced on mild steel. giving a pickled and etched appearance.

AISI 304L stainless steel is unsuitable in active sulfate reducing bacteria environments (SRB), and even AISI 316L experienced distinct pitting and intergranular corrosion initiation.

Alloys high in sulfur are inferior to low sulfur alloys in active SRB environments."

COMMENTS OF THE REVIEWER

This study was conducted under good conditions for the growth of sulfate reducing bacteria (SRB) and under less favorable conditions for the materials to attain or maintain corrosion resistance. The tests were conducted in an oxygen free environment and in a bacterial growth medium; conditions that enhance bacterial growth but that can degrade metal passivity. It is possible that conditions in the nuclear waste storage repository in locations where SRB attack would be a problem could be similar or related to the conditions of these tests, especially with regard to the absence of oxygen. SRB would not be expected to be a problem in the oxygenated environment of the planned Yucca Mountain Nevada tuffaceous rock repository, but oxygen could be absent or depleted in crevices, cracks and similar areas. These conditions would need to be determined and additional tests should be run to determine whether the "worst case" situation described in this paper would actually occur.

The experiments described in this paper appear to have been conducted carefully, and the results, that all of the alloys studied are susceptible to attack by the SRB, should not be ignored. The ranking of materials studied in terms of decreasing pit density is Sandvik > mild steel > AISI 409 SS > 3Cr12A > 3Cr12B > 3Cr12 > AISI 304L SS > AISI 316L SS > AISI 316 SS. Results in the weight loss data were less striking, but the Sandvik suffered the greatest loss (8 mg/cm²) and the 316 SS had the lowest weight loss (2.62 mg/cm²).

APPLICABILITY OF DATA TO LICENSING

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

- (a) Relationship to Waste Package Performance Issues Already Identified
 - 2.2.4.4 Will microbes affect corrosion of the waste package container, and if so, how?
- (b) New Licensing Issues
- (c) Comments Related to Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA.
For the NNWSI Project, U.S. DOE.

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

Van Konynenburg, R. A., Smith, C. F., Culham, H. W., and
Otto, C. H., Jr., "Behavior of Carbon-14 in Waste
Packages for Spent Fuel in a Repository in Tuff,"
UCRL-90855, November 1984.

DATE REVIEWED: 6/7/89; Revised 8/8/89

PURPOSE

The authors state in the introduction that "Our laboratory was asked to perform mass spectrometric and radiometric analyses of gas samples taken from spent fuel storage canisters in order to determine whether any fuel rods had ruptured." "This paper discusses the initial results obtained and the ramifications for the storage of spent fuel in a potential repository in Tuff."

KEY WORDS

Data analysis, experimental data, gaseous radionuclides escape, spectroscopy, laboratory, air, N₂, O₂, Ar, He, CO₂, CO, N₂O, ¹³CO₂, ⁸⁵Kr, ¹⁴C, ¹⁴CO₂, ¹³C, high temperature, stainless steel, spent-fuel-rod (PWR), gas escape, thermal instability.

CONTENTS

Text: 8 pages, 2 tables, and 22 references.

AMOUNT OF DATA

Table 1. Spectrometric and Radiometric Analyses.

Table 2. Calculated Gas Volumes and Releases.

TEST CONDITIONS

1. Materials: "15x15 PWR spent fuel rod assembly." "It consists of UO₂ fuel pellets inside Zircaloy-4 tubes, held in place by type 304 stainless steel orifice plates

and Inconel 718 spacer grids." "After removal from the reactor the assembly was stored in a water pool for less than 2 years." Then, the assembly "was sealed inside a helium-filled canister, and was used in a silo-type fuel storage test for about 4 years."

2. Specimen Preparation: "The assembly was removed from its canister and inspected, and two fuel rods were removed. The assembly was then placed in the Fuel Temperature Test (FTT) stand."
3. Environments: "The canister of the FTT was filled with air and the temperature was raised to 275°C and was programmed to decrease slowly with time." The dose rate was 10⁴ rd/h.

UNCERTAINTIES IN DATA

"The CO₂ analyses for samples #26 and #34 are somewhat suspect because of air leaks into the samples during storage prior to analysis."

DEFICIENCIES/LIMITATIONS IN DATABASE

"A comparison of this value with the 10CFR60 release limit of 10⁻⁵ per year from the 'engineered system' shows that it will be important to carefully define the 'engineered system' and to take account of the time distribution of lifetimes of the canisters to meet this requirement, the 10CFR60 limit."

CONCLUSIONS OF AUTHOR

1. About 1.5 mCi of ¹⁴C was rapidly oxidized and released as gas from the external surface of a PWR spent fuel assembly stored in air at 275°C and producing a radiation field of about 10⁴ rd/h.
2. An additional 0.3 mCi was released as gas after one of the 204 fuel rods was breached, but it is likely that most of this also came from the external surface of the assembly. Radiometric ¹⁴C analysis should be performed directly on fuel rod gas to check this conclusion.
3. The initial gaseous release would not exceed the limit of 40CFR191. Further study is needed on slower releases of ¹⁴C.
4. This gaseous release is large enough that a broad definition of the 'engineered system' in 10CFR60 may be necessary, and account will have to be taken of the time distribution of lifetimes of the canisters, in order to meet the requirement of this regulation.

COMMENTS OF REVIEWER

1. There is a limited amount of experimental data on the release of the ^{14}C from spent fuel; therefore, the authors question the validity of conclusions derived from their own calculated results.
2. In discussing the present results in light of 10CFR60 (or 40CFR191), the authors do not consider the container of the waste package in the repositories as a possible source of ^{14}C . Only the fuel itself was considered, and other sources should be considered.
3. In agreement with these authors, the reviewers recommend that radiometric analysis of ^{14}C should be conducted directly on fuel-rod gases.

RELATED HLW REPORTS

1. R. A. Van Konynenburg, C. F. Smith, H. W. Culham, H. D. Smith, "Carbon-14 in Waste Packages for Spent Fuel in a Tuff Repository," Lawrence Livermore National Laboratory, UCRL-94708, October 1986.

APPLICABILITY OF DATA TO LICENSING

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

- (a) Relationship to Waste Package Performance Issues Already Identified
 - 2.3 When, how, and at what rate will radionuclides be released from the waste form?
- (b) New Licensing Issues
- (c) Comments Related to Licensing

AUTHOR'S ABSTRACT

Analysis of gas from a heated air-filled canister containing a spent fuel assembly before and after rupture of a fuel rod shows that about 1.5 mCi of ^{14}C from the external surface of the assembly was rapidly oxidized and released as $^{14}\text{CO}_2$ in excess oxygen at 275°C and 104 rad/hr. After rupture, an additional 0.3 mCi was released, probably also from the external surface. The total ^{14}C inventory in the entire 15x15 rod assembly including structural hardware is estimated to be 690 mCi. These measurements indicate that account will have to be taken of the time distribution of lifetimes of the canisters, and a broad definition of the "engineered system"

may be necessary, in order to meet 10CFR60 requirements with spent fuel in a repository in tuff.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data
Westinghouse Hanford Company, Pacific Northwest
Laboratories, Richland, WA. For the NNWSI Project, U.S.
DOE.

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

Wilson, C. N.
"Summary of Results from the Series 2 and Series 3 NNWSI
Bare Fuel Dissolution Tests"
UCRL-21013, November 1987.

DATE REVIEWED: 6/25/89

PURPOSE

"Tests have been conducted at Westinghouse Hanford Company in support of the NNWSI Project Waste Package Task at Lawrence Livermore National Laboratory to study the dissolution behavior of spent fuel in groundwater under NNWSI-relevant conditions." "Although spent fuel specimens in defected and undefected cladding were tested in both Series 2 and Series 3, only results from the bare fuel tests are discussed in this paper."

KEYWORDS

Experimental data, leaching, x-ray diffraction, solution analysis (not specified), laboratory, air, J-13 water, Cl, Fe, Ca, Cr, K, Mg, Na, Ni, Si, F, NO₃, SO₄, HCO₃, fuel rod segment irradiated in HBR and Turkey Point PWR, ambient temperature, dynamic (flow rate given) 40 l/year, high temperature, spent fuel (PWR), ²⁴¹Am, ¹³⁷Cs, ¹²⁸I, ²³⁹Pu, ²⁴⁰Pu, ⁹⁹Tc, ¹³⁴C, ⁹⁰Sr, ¹⁴C, ²²³Rn, radionuclide release, leaching (spent fuel).

CONTENTS

This paper consists of 11 pages containing abstract, 8 figures, 3 tables, and the following content

CONTENTS

NUMBER OF PAGES

| | |
|--|-----|
| Introduction | 0.5 |
| Test Description | 1.0 |
| Results and Discussion | 7.0 |
| Principal Observations and Conclusions | 0.5 |

AMOUNT OF DATA

There are 8 figures and 3 tables. One figure shows the experimental set-up and several other figures show concentration versus time (15 to 34 months) for uranium (U, plutonium ($^{239}+^{240}\text{Pu}$), americium (^{241}Am) and technetium (^{99}Tc). One table shows ^{14}C and ^{129}I in solution at the end of Cycle I (~200 days)

TEST CONDITIONS

Materials: Bare Spent Fuel

Specimen Preparation: "Specimens prepared from fuel rod segments irradiated in the H. B. Robinson (HBR) and Turkey Point pressurized water reactors."

Environments: "The Series 2 tests were conducted in NNWSI reference J-13 well water using unsealed fused silica vessels under ambient air (25°C) hot cell conditions. The Series 3 tests were similar to the Series 2 tests except that the Series 3 tests were conducted in sealed 304L stainless steel (304 in cycle 1) vessels at 85°C (one Series 3 test was run at 25°C)."

UNCERTAINTIES IN DATA

Not stated.

DEFICIENCIES/LIMITATIONS

"Based on a water flux of about 40 l/year per 3140 Kg UO_2 ,"
"the data appear quite favorable for meeting the 0.1 Ci/MTHM EPA 10,000-year cumulative release limits for ^{239}Pu , ^{240}Pu and ^{241}Am with a high degree of conservatism."

" ^{99}Tc releases greater than 1 part in 100,000 per year could occur for some time from saturated failed waste packages."

"The data did not indicate that ^{129}I was released to the atmosphere in the Series 2 tests."

CONCLUSIONS OF AUTHOR

1. Actinide concentrations generally saturated, and often decreased, during test cycles.

2. Uranium concentrations tended towards about 1 to 2 $\mu\text{g/ml}$ in the Series 2 tests and about 0.1 to 0.4 $\mu\text{g/ml}$ in the Series 3 tests, with the lowest concentrations observed in the 85°C Series 3 tests.
3. Formation of a Ca-Si-U containing secondary phase identified as uranophane was observed in the 85°C Series 3 tests.
4. Activities of the three major alpha emitting actinides ^{241}Am , ^{239}Pu , and ^{240}Pu dropped below a pCi/ml in the 85°C Series 3 tests, which are favorable data for meeting release requirements for these important radionuclides.
5. After an initial fast release at the beginning of Cycle 1, continuous preferential releases of ^{99}Tc and ^{137}Cs occurred with the rates of release greater at 85°C than at 25°C. Continuous release of these soluble radionuclides is thought to result primarily from dissolution of fission product phases which segregate to the grain boundaries during irradiation.
6. Relatively high C-14 activities were measured in the Series 3 tests and in the TP-3-85 test in particular. Much of the ^{14}C released in the unsealed Series 2 tests may have been lost to the atmosphere as CO_2 . The data did not indicate that ^{129}I was released to the atmosphere in the Series 2 tests.

COMMENTS OF REVIEWER

1. This report provides us with important data regarding the release of various radionuclides from spent fuel, assessing the government rules set by NRC or EPA.
2. In assessing the EPA or the NRC rules of radionuclides release, it is recommended that the tested flow rate, 40 l/year, be clarified to be of a typical repository condition and how to show the present data could be changed if the tests were performed at realistically lower flow rates.
3. The potential involvement of oxidation during the experiment needs to be ruled out in drawing conclusions on the performance of waste packages under the repository conditions. Such oxidation may come from the fuel sectioning and from the time of test cycle change.

RELATED REPORTS

1. C. N. Wilson, "Results from Cycles 1 and 2 of NNWSI Series 2 Spent Fuel Dissolution Tests," HEDL-TME 85-22, Hanford Engineering Development Laboratory, Richland, WA, May 1987.
2. C. N. Wilson and H. F. Shaw, in Scientific Basis for Nuclear Waste Management X, edited by J. K. Bates and W. B. Seefeldt (Materials Research Society Symposium Proceedings 84, Materials Research Society, Pittsburgh, PA, 1987) pp. 123-130.
3. J. O. Barner, "Characterization of LWR Spent Fuel MCC-Approved Testing Material ATM-101," PNL-5109, Pacific Northwest Laboratory, Richland, WA, June 1984.
4. R. B. Davis and V. Pasupathi, "Data Summary for the Destructive Examination of Rods G7, G9, J8, I9 and H6 from Turkey Point Assembly B17," HEDL-TME 80-85, Hanford Engineering Development Laboratory, Richland, WA, April 1981.

APPLICABILITY OF DATA TO LICENSING

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

- (a) Relationship to Waste Package Performance Issues Already Identified
 - 2.3.2.1.2 What are the rates of dissolution associated with the potential waste form dissolution mechanisms?
- (b) New Licensing Issues
- (c) Comments Related to Licensing

AUTHOR ABSTRACT

The Nevada Nuclear Waste Storage Investigations (NNWSI) Project is studying dissolution and radionuclide release behavior of spent nuclear fuel in Nevada Test Site groundwater. Specimens prepared from pressurized water reactor (PWR) fuel rod segments were tested for multiple cycles in J-13 well water. The Series 2 tests were run in unsealed silica vessels under ambient hot cell air (25°C) for five cycles for a total of 34 months. The Series 3 tests were run in sealed stainless steel vessels at 25°C and 85°C for three cycles for a total of 15 months. Selected summary results from Series 2 and Series 3 tests with bare fuel specimens are reported.

Actinide concentrations tended to saturate and then often decreased during test cycles. Uranium concentrations in later test cycles ranged from 1 to 2 $\mu\text{g}/\text{ml}$ in the Series 2 tests versus about 0.1 to 0.4 $\mu\text{g}/\text{ml}$ in Series 3 with the lowest concentrations occurring in the 85°C tests. Formation of a calcium-uranium-silicate phase identified as uranophane in the 85°C Series 3 tests is thought to have limited uranium concentration in these tests. ^{241}Am , ^{239}Pu and ^{240}Pu activities measured in filtered solution decreased to less than 1 pCi/ml in the 85°C tests. Preferential release of fission products Cs, I, Sr and Tc, and activation product C-14, was indicated relative to the actinides. ^{99}Tc and ^{137}Cs activities measured in solution after Cycle 1 increased linearly with time, with the rate of increase greater at 85°C than at 25°C. Continuous preferential release of soluble fission products is thought to result primarily from the dissolution of fine particles of fission product phases concentrated at the grain boundaries.

Appendix C. NIST Review of the "Final Report of the Defense High-Level Waste Leaching Mechanisms", PNL-5157, August 1984

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Pacific Northwest Laboratory, Richland, Washington 99352.

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

Mendel, J. E., Compiler,
"Final Report of the Defense High Level Waste Leaching
Mechanisms Program"
PNL-5157, August 1984. Available from NTIS.

DATE REVIEWED: 7/27/89

PURPOSE

Purpose of Program:

"The objective of the leaching mechanisms program was to determine the dominant leaching mechanisms for defense waste glass and to evaluate the effects of some major potential environmental parameters upon the leaching mechanisms."

Purpose of Review:

The NIST has reviewed the "Final Report of the Defense High-Level Waste Leaching Mechanisms Program", PNL-5157, which is a 1984 literature review on glass leaching behavior of nuclear-waste glasses that have been proposed for use in the vitrification of high level waste (HLW). The report consists of seven chapters and each chapter was prepared by one or more of seven reviewers. The PNL-5157 report was made under the direction of the Materials Characterization Center (MCC). Chapter topics are given below:

- (1) Mechanism of Defense Waste Glass Corrosion
- (2) Surface Layer in Leached Borosilicate Glass HLW Forms
- (3) Environmental Interactions
- (4) Dissolution of Specific Radionuclides
- (5) Radiation Effects
- (6) Phenomenological Models of Nuclear Waste Glass Leaching
- (7) A Computer Code PROTOCOL for a Numerical Simulation of Glass Dissolution

For each chapter, the NIST has conducted a review to identify the following categories of information: (1) the type of

literature, (2) materials used, (3) test conditions, (4) analysis methods, (5) uncertainties in data, (6) deficiencies/limitations in data base, and (7) conclusions. A summary of comments given by NIST reviewers of these chapters, with appropriate recommendations, is presented below in the order indicated above for the seven sections of the NIST reviews. For more details on any one chapter, see the NIST review of that chapter.

Since the publication of this report (PNL-5157) in 1984; MCC has obtained additional results. The reader is referred to their reports and to reports from SRI, WVDP, Vitreous State Laboratory at the Catholic University of America.

KEY WORDS

Literature review, leaching, solubility, PROTOCOL, microscopy (light, electron, SEM, etc.), spectroscopy, surface film, weight change, x-ray diffraction, fluorometric uranium, laboratory, Yucca Mountain, deionized, simulated groundwater, HCl, NH₄OH, Stripa, Cl⁻, F⁻, CO₃²⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, OH⁻, NH₄⁺, tuff, alpha radiation field, gamma radiation field, beta, acidic solution (pH <7), ambient pressure, ambient temperature, basic (alkaline) solution (pH >7), dynamic (flow rate given) 0.1 to 10 ml/h, high pressure, high temperature, neutral solution (pH = 7), static (no flow), glass (defense waste reference glass), defense high-level waste (DHLW), Np237, Pu239, U, groundwater, DI water, leaching (radiation enhancement), matrix dissolution (glass).

CONTENTS

This report consists of an introduction, a summary and conclusions, and the following contents:

Chapter 1 contains 63 pages, 28 figures, 21 tables, 90 references.
Chapter 2 contains 37 pages, 34 figures, 7 tables, 30 references.
Chapter 3 contains 43 pages, 12 figures, 13 tables, 98 references.
Chapter 4 contains 49 pages, 52 figures, 7 tables, 41 references.
Chapter 5 contains 18 pages, 9 figures, 8 tables, 48 references.
Chapter 6 contains 16 pages, 8 figures, 0 tables, 44 references.
Chapter 7 contains 35 pages, 35 figures, 8 tables, 15 references.

Appendix A: Reference Materials contains 2 pages, 2 tables, 2 references.

Appendix B: Use of PROTOCOL contains 7 pages, 1 table, 1 reference.

Appendix C: Leaching Mechanisms in Polyphase Ceramic High-Level Nuclear Waste Forms contains 28 pages, 22 figures, 11 tables, 11 references.

AMOUNT OF DATA

The report "PNL-5157" comprehensively covers experimental efforts, modeling studies and a review of the literature related to leaching of nuclear waste glass, which is glass loaded with radioactive waste.

Emphases are on the simulated nuclear-waste glasses in the repository environments, including glasses containing ^{239}Pu , ^{237}Np or U. Control studies performed in commercial glasses were also reviewed. Finally, in relation to safe performance of glass over geological times, the nature of ancient and natural glasses was evaluated.

TEST CONDITIONS

This extensive review covers various glass shapes that had been tested. The forms of the glasses are either monoliths or powders. The ratio of surface area to glass leachate volume, as covered in these tests, ranges from 10^{-5} to 2300-m^{-1} . For the surface of the monolith, preparation of the surface is very important. The surfaces were normally polished with Si-C papers, but inadequate documentation on surface preparation given in this document seems to have left this important variable at times uncontrolled.

This 1984 publication (PNL-5157) did not refer to the definitive study by Kingston et al. (1984)¹, but the MCC has revised MCC-1 and the revision includes changes that can be attributed to the Kingston study. That revision to MCC-1 was made after the 1984 publication of PNL-5157.

The flow conditions for leachates are either static or dynamic conditions. In dynamic tests, continuous flow of the leachate was used to simulate high flow rates of groundwater. In another test, pulsed replenishment of the leachate was used to simulate the low flow rates expected to be present in some

¹ H.M. Kingston, D.J. Cronin, and M.S. Epstein, "Investigation of a Precise Static Leach Test for the Testing of Simulated Nuclear Waste Materials", Nuclear and Chemical Waste Management, v5, p3-15, 1984.

candidate repositories. Normally, the flow rates tested ranged from 0.1 to 10 ml/h. The testing temperatures ranged from 40 to 93°C, at ambient pressures, for times of up to 12 months.

The pH and Eh conditions of the leachate are respectively from one to 11 and from -10 to -80 mv. The leachates are deionized (DI) water, hydrochloric acid (HCl), ammonium hydroxide (NH₄OH) or simulated groundwater, including Hanford, Tuff and Stripa constituents. Leachates are either air-saturated, nitrogen-saturated or silicated. Environmental effects due to waste package components (other than glass) were also considered. These components include iron, stainless steels, and other secondary components such as backfill materials, each of which might be present in the leachates. In the case of radiation tests, alpha, beta and gamma were all considered for the structural damage effects as well as for radiolytic effects. Besides using these experimental conditions, one- and/or two-dimensional simplification was used in the modeling as a geometric description of the leaching system.

The leach rates are normally measured as the total mass loss per unit area per unit time (mass/A/t). The total mass loss was determined by atomic absorption (AA) or inductive coupled plasma spectroscopy (ICP); in addition, many other techniques were used for surface analyses, including SEM, SIMS, XPS, SIPS, AES, SAM and XRD. For radiation studies, actinide doping methods or external heavy ion and/or neutron irradiation were utilized. In the modeling efforts, solute diffusion was extensively used, and modifications were made in conventional leach models by taking into account the leachate saturation and the subsequent precipitates.

UNCERTAINTIES IN DATA

The presented data were examined carefully for uncertainties including error bars (or tolerance limit of each data set), and the drifting of experimental conditions such as pH was noted. To estimate reproducibilities, the averages of at least two determinations were given. Normally, in PNL-5157, this reliability information is not very extensive, especially in modeling, as for example, for the reaction rate constants used in the model: As a consequence of using uncertain reaction-rate constants, the exponent of the power-law leach-kinetics varied from -0.2 to 0.6, which may be unacceptable for most purposes.

DEFICIENCIES/LIMITATIONS IN DATABASE

Each chapter rarely addresses the deficiencies/limitations in the data base (used for PNL-5157) in relation to any licensing

application issues. These issues would emphasize the leaching behavior of waste glass over extended (geological) times. Such an example is the determination of thermodynamic equilibrium for the solubility consideration: The state of seemingly thermodynamic equilibrium can be simply a balance state between dissolution and precipitation of the waste glass under repository conditions. See below for more details, which are given in the Conclusions section of this review.

CONCLUSIONS

Refer to Conclusions for each chapter and to comments of this review.

RELATED REPORTS

1. Sales, B. C., White, C. W., and Boatner, L. A., "Application of Ion Implantation and Backscattering Techniques to the Analysis of Nuclear Waste Glass Corrosion," Mater. Lett. (Netherlands), Vol. 2(1), 1-5, 1983.
2. Sales, B. C., Begun, G. M., White, C. W., Boatner, L. A. Green, P. H., and Watson, D. M. (Eds.), "Surface Layer Formation on Corroded Nuclear Waste Glasses, Oak Ridge Nat. Lab. Report No ORNL-6128 213-214, March 1985.

COMMENTS:

Summary:

The following is a summary of views of the NIST review groups for 7 chapters of PNL-5157.

This report, PNL-5157, was put together by the MCC (PNL-Battelle). No effort was made to link these chapters together. The objective was, "to determine the dominant leaching mechanism for defense waste glass". The objective has not been achieved. In itself this result is not surprising; the mechanism probably is very complicated. However, the report should state this.

Throughout the document no mention is made of several papers concerning the process of glass leaching by a group under L. A. Boatner at the Oak Ridge Laboratory. This group, using Rutherford Back Scattering, has shown that the attack of water (or brine) on glass is a discontinuous process: The various impurities or mixed-in elements move to the surface. At the same time the SiO₂-glass structure is weakened, and after periods of less than one day (6-10-14 hours!) this weakened "surface layer" sloughs off into the liquid and a new "virgin"

surface is exposed to the liquid. Certainly any report about the leaching mechanism of glass should pay attention to these findings.

In the present report the experimental approach is mainly chemical; one measures what is dissolved in the leachate. Additional SEM measurements are performed on a long-time scale and with an accuracy of the order of 0.1 μm . RBS (Rutherford Back Scattering) experiments can be performed on a time scale of hours and a dimensional scale of 5-15-nm. This technique makes it possible to get a rather accurate picture of what happens in the surface layers.

By performing the experiments after periods of 6, 12, etc. hours, one obtains information about the kinetics of the process.

The leach rates are extremely low regardless of the glass compositions at pH of 7 to 9, and temperatures from 40 to 93°C and low flow rates. A comprehensive coherent picture of glass leaching is not now available.

Other effects of solution chemistry include those associated with iron and/or backfill-materials. These materials may be present in various components of a repository. They tend to increase the leach rates by forming precipitates. Species dissolved in the groundwater tend to decelerate the leach rates, because their presence brings the leachates closer to their solubility limits.

While much of the above discussion assumes conditions in which saturation concentrations have not been met, complications do arise from saturated leachates. In addition, a list of other complications to the development of a mechanistic understanding of the leaching process would include the following:

- (1) As leaching progresses, the pH changes.
- (2) The presence of iron ions will be to alter the solution Eh and/or oxic conditions. This will affect the leach rates. The Eh conditions were found to be important for the long-lived Tc and transuranic species, because the various valence states of these species have different solubilities.
- (3) The surface layer becomes altered and plays an important role in the leaching process.
- (4) The surface layer grows in the amorphous state with pits and crystalline deposits and its formation and growth are most greatly affected by solution chemistry as discussed above, i.e. it forms from products coming from solution rather than those coming from the glass itself.
- (5) Colloidal-sized particles form in the leachates; this is particularly important for Tc and transuranic species.

The role of the altered layer has not been studied and understood adequately well to make it possible to prevent or greatly retard leaching by careful control of glass chemistry. It would seem that leach rates could be greatly decreased by use of tailored glass compositions, which promote (for specific environments) the formation of an alteration layer that prevents further leaching.

The level of the radiation field expected to be present in a waste package sufficient to produce structural damage in glass as well as in the host rocks, and whether the state of thermodynamic equilibrium is obtained or not, is an important question for the prediction of long-term glass leaching behavior. When precipitates go, either on glass surfaces or in solutions, the solutions are not necessarily in a state of thermodynamic equilibrium. They can be simply in a balanced state between dissolution and precipitation of the available solids in the solutions. This is a dynamic state that can be terminated (at a limiting condition) in a state of thermodynamic equilibrium, e.g. at the solubility limit for a precipitate; at that limit it is presumed that the system is in equilibrium. Both again accelerate leach rates.

The development of models and computer codes, as presented in PNL-5157 for glass leaching, includes the classical approach in a dilute solution, the interaction with the leachate concentration, solubility effects, and a model for dispersion to the biosphere. However, the efforts presented in this publication are successful only in forming a skeleton/foundation which needs further polishing. Of course, deeper understanding of detailed leaching phenomena will be required to do successful modeling.

APPLICABILITY TO DATA TO LICENSING

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

- (a) Relationship to Waste Package Performance Issues Already Identified
- 2.3 regards when, how, and at what rate, will radionuclides be released from the waste form.
 - 2.3.1 regarding physical, chemical and mechanical properties of the waste form with time
 - 2.3.2 regarding solubility of the waste form under repository conditions
 - 2.3.2.1 regarding possible dissolution mechanisms of the waste form under repository conditions
 - 2.3.2.1.1 which waste form dissolution mechanism or mechanisms are most likely?
 - 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?

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

2.2.4.2.1 concerning the predicted rate of radiolytic generation of hydrogen, oxygen and other species due to gamma radiation in the vicinity of the waste package containers.

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

6.5 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

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.

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

Barkatt, A., Macedo, P., Montrose, C.
Mendel, J. E., Compiler
"Final Report of the Defense High Level Waste Leaching Mechanisms Program, Chapter 1, Mechanisms of Defense Waste Glass Corrosion: Dissolution of Glass Matrix"
PNL-5157, August 1984. Available from NTIS.

DATE REVIEWED: 2/22/87; Revised 11/12/87.

KEY WORDS

Data analysis, experimental data, literature review, theory, leaching, leachate analysis by ICP spectrometry, atomic absorption, calorimetry, laboratory, air, CO₂ free air, deionized, simulated groundwater, acid solution (pH <7), basic (alkaline) solution (pH >7), dynamic (flow rate given), high temperature, acidic solution buffered by CO₂, glass, SRL-TDS 131m PNL-76-68.

TYPE OF DATA

Experimental data and literature review dealing with glass corrosion, including review of various types of corrosion tests.

MATERIALS/COMPONENTS

The materials studied were simulated nuclear waste glasses. Test glasses included SRL TDS-131, Defense Waste Reference Glass (DWRG), PNL 76-68 glass, PGM glass (a high-silica borosilicate defense waste glass), and CUBS glass (a high-silica borosilicate glass).

TEST CONDITIONS

The glass corrosion studies reviewed cover a wide variety of experimental conditions to help elucidate the basic mechanisms involved.

Tests were conducted on both monolithic and powdered specimens of the two glasses. Corrosion tests included static tests,

continuous flow and pulsed flow tests, constant medium tests and hydrothermal tests.

Variables included aqueous environment (deionized) water, simulated groundwater, buffered DI water, temperature, the ratio of glass surface area to solution volume (S/V ratio), and contact time.

METHODS OF DATA COLLECTION/ANALYSIS

The corrosion data is presented as total mass loss per unit area per unit time, or in terms elemental mass loss. Elemental mass loss is determined from measurement of elemental concentrations in the leachate. Leachate concentrations were determined by ICP spectrometry, atomic absorption spectrometry and colorimetry. Also given are pH measurements. Surface layer thickness and composition were determined by SEM/EDX. The corrosion data reported as a function of time or flow rate.

AMOUNT OF DATA

Twenty-one tables are given showing glass composition, corrosion data for individual glasses under specific conditions, comparison of various glasses under the same conditions, and comparison of various test methods. Twenty-eight figures are given showing configurations of various test methods, corrosion data for specific glasses under specific conditions, and comparison of results when different parameters are varied.

Tables

- 1 Composition of Nuclear Waste Borosilicate Glasses
- 2 Correlation of Exchanged Fraction and Exchange Frequency, PNL 76-68 Glass, 70°C
- 3 Comparison of Continuous-Flow and Pulsed-Flow Leach Tests in Deionized Water at 90°C
- 4 Dynamic Leach Tests on SRL TDS-131 in Deionized Water at 70°C
- 5 High Dilution Test at Various Temperatures SRL TDS-131 Glass, Normalized Leach Rates
- 6 Comparison Between TDS-131 and DWRG, Leach Data in DI Water, Modified IAEA 90°C
- 7 Effects of Glass and Leachant Composition on the Results of Flow Tests at 70°C
- 8 Solubility Tests on Defense Waste Glass, 10 g of -60 +200 Mesh Powder in DI water, 70°C, 360 days
- 9 Dynamic Leach Tests on DWRG, 70°C
- 10 Results of Dynamic Leach Tests on DWRG in DI Water at 90°C

- 11 Effects of Ground Water and of Ductile Iron on DWRG Leach Rates in Dynamic Leach Tests, Monolithic Samples, 90°C
- 12 Effects of Temperature on DWRG Leach Rates in Dynamic Tests, Monolithic Samples
- 13 Speciation of Leached Components of DWRG in Dynamic Tests, 90°C
- 14 Comparison of the Results of MCC-1 and Dynamic Leach Tests on DWRG, 90°C, Monolithic Samples
- 15 Molar Compositions of the Glass and of the Saturated Leachant (Relative to Boron) and Resulting Surface Compositions for TDS-131 and DWRG
- 16 Experimental Run Conditions for the Reaction of DWRG with DI Water Under Hydrothermal Conditions
- 17 Solution Analysis for the Reaction of DWRG with Water, Concentrations in mg/kg Water, 0.10 gm Water, One Face Polished
- 18 Solution Analyses for the Reaction of DWRG with Water, Concentration in mg/kg water, 0.01 gm water, both faces polished
- 19 Dynamic Leach Tests on PNL 76-68 at 70°C
- 20 Dynamic Leach Tests on PGM Glass at 70°C
- 21 Dynamic Leach Tests on CUBS and DWRG, DI Water, 70°C

Figures

- 1 Experimental Configuration of Continuous-Flow Leach Test
- 2 Experimental Configuration of Pulsed-Flow Leach Test
- 3 Results of Frequent-Exchange Tests on SRL TDS-131, DI water, 90°C
- 4 Effects of Flow Rate on Leachate Concentrations, Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131 Glass
- 5 Effects of Flow Rate on the Release Rates of Si and Na in Continuous-Flow Leach Tests on TDS-131 and DWRG
- 6 Effects of Flow Rate on Leachate pH Measured as a Function of Corrosion Time in Continuous-Flow Leach Test on TDS-131 Glass
- 7 Effects of Flow Rate on Total Mass Loss Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131 Glass
- 8 SEM-EDS of 28-Day Corroded Samples Exposed to Water at Several Flow Rates
- 9 Thickness of Leached Layers Observed in 28-Day Corroded Samples Exposed to Water at Several Flow Rates
- 10 Effects of Flow Rate and S/V on Total Mass Loss Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131
- 11 Dependence of Leachate Concentration on Total Exposure Time in a Constant-Flow-Rate Leach Test
- 12 Dependence of Stabilized Leachate Concentrations on Flow Rate in a Flow Test

- 13 Dependence of Leach Rates on Flow Rate in a Flow Test
- 14 Relative Leach Rates of Various Glass Components in a Flow Test
- 15 Results of Dynamic Leach Test on SRL TDS-131, DI Water, 70°C, Normalized Concentration versus $T_r(S/V)$
- 16 Results of Dynamic Leach Test on SRL TDS-131, DI Water, 70°C, Leach Rate Versus Contact Time
- 17 Results of Dynamic Leach Test on SRL TDS-131, DI Water, 70°C, Intermediate Flow Rate, Concentration Versus Total Exposure Time
- 18 Results of Dynamic Leach Tests on SRL TDS-131, DI Water, 70°C, Slow Flow Rates, Concentration Versus Total Exposure Time
- 19 Results of Frequent-Exchange Tests on SRL TDS-131 in DI Water at Various Temperatures
- 20 Concentrations of Si and Na Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131 Glass
- 21 Leachate pH Values Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on DWRG
- 22 Normalized Total Mass Loss Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on DWRG
- 23 Results of Dynamic Leach Tests on DWRG, Ground Water, 70°C, Intermediate Flow Rates, Concentration Versus Total Exposure Time
- 24 Results of Dynamic Leach Tests on DWRG, DI Water, 70°C, Intermediate Flow Rates, Concentration Versus Total Exposure Time
- 25 Results of Dynamic Leach Tests on DWRG, DI Water, 70°C, Slow Flow Rates, Concentration Versus Total Exposure Time
- 26 Results of Dynamic Leach Tests on DWRG, DI Water, 90°C, Normalized Concentration Versus $T_r(S/V)$. Data Points in Parentheses Obtained in the Presence of Iron.
- 27 Results of Dynamic Leach Tests on DWRG, DI Water, 90°C, Leach Rate (fractional loss rate) Versus Contact Time (equivalent flow rate)
- 28 T-T-T Plot of the Formation of Crystalline Products (DWRG) Flow Rate

UNCERTAINTIES IN DATA

Error bars are included on some figures, but not all. Tables of corrosion data make no reference to the precision or accuracy of the data. The authors state that the pulsed flow experiments were performed at least in duplicate, blank tests were carried out, and the analytical accuracy in the determination of the major components in solution was within +/- 10 percent.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

"At sufficiently low flow rates the release rate of waste glass matrix components is directly proportional to flow rate."

"The concentration of components in the leachate is nearly independent of flow rate."

"In the case of the Defense Waste Reference Glass, the pH rise is moderate and solubilities do not exhibit a very large increase even at the slowest flow rate."

"At sufficiently high flow rates, the release rate becomes constant, limited by the kinetics of the dissolution of the glass matrix. But, the high flow rates are highly unlikely in a geologic repository."

COMMENTS OF REVIEWERS

Introductory Remarks

The stated assignment for Chapter 1 was to "describe the leaching of the glass matrix as a function of glass composition, leachant flow rate, temperature and leachate composition." Since the goal of the work is prediction of long-term leach rates, it is implicit that "describe" has to be quantitative. The chapter does not succeed in this respect; it does point the way with varying degrees of certainty.

Two key conclusions are inescapable. One is that under so-called, "normal" conditions, the repository parameters will be a major factor controlling the leach rate. The other is that there is no clear definition of "abnormal," or worst case conditions, and hence no coherent study of their effects on leaching.

The chapter is poorly organized and, as a result, not easy to read or understand. This is due partly to the fact that it seems to be a collection of different experiments with no coherent framework binding them together, and partly to the fact that relatively simple concepts are stated in complex ways. Better reviews of glass leaching are available, including those listed below under RELATED HLW REPORTS (Clark et al., Jantzen and Plodinec).

Glass Composition Effect

The qualitative effects of glass composition on leach rates are discussed, but there is little if any data to predict quantitative effects. Of course, it must be recognized that this task becomes very complex when dealing with glasses which contain 20 to 30 different components. (Even if the "leach system" could be simply described, which it cannot.)

The authors have pointed out that glass corrosion rates are extremely dependent on the glass composition and that seemingly small changes in composition can have a very large effect on corrosion rates. This is important because of the compositional variations that exist in the current holdings of defense high-level waste. However, there is little information in the report to indicate how these chemical parameters are to be changed to permit formation of more durable glasses. The limited quantitative nature of the recorded observations can be appreciated by noting that the chapter summary includes only one statement regarding compositional effects, i.e., that high-silica glasses show a linear relationship between flow rate and leach rate up to greater flow rates than low-silica glasses.

Throughout the chapter there are various other compositional effects noted, most of which are recorded in the general glass durability literature. These include the fact that an increase in Al_2O_3 increases solubility in alkali and acid systems, but decreases neutral system solubility, and that increases in alkali tend to drive the equilibrium pH higher.

The glass composition results are based on studies of five synthetic nuclear-waste compositions, plus some generalizations about natural and ancient glasses. Because of the sensitivity to compositional variations, inclusion of a broader range of glass compositions would have made this study more useful. It appears that the synthetic glasses were not selected to optimize a composition study, but rather happened to be available or already studied to some degree. The statement in the report that "the difference in composition between SRL TDS-131 (44% SiO_2 and 13% Na_2O) and DWRG (50% SiO_2 and 8% Na_2O) is not very large" is very surprising. Most glass chemists would perceive a large difference between these glass compositions. The natural and ancient glasses fit the "overall" picture quite well as is generally recognized, but really provide only supporting evidence.

Compositional variables are stated in terms of weight percent, although it is customary among glass chemists to state them in mole percent or cation percent in order to appreciate better the significance of atomic structure.

Only one page, (section 1.6.4) addresses systemization of effects of glass compositions. The following quotes need no further elaboration.

"It is not possible to obtain a general dependence of "durability," on glass composition since leach rates strongly depend on test conditions." "At the present time, extensive data on compositional effects on the durability of glasses are very limited."

"....Attempts at systemization and generalization of compositional effects on glass durability can be fruitful and both experimental and theoretical studies in this area should be pursued."

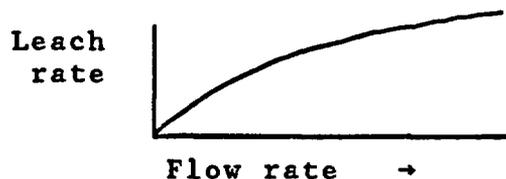
It must be concluded that the quantitative effects of glass composition on leaching have not been determined. It could be done with a great deal more work. The question is whether this effort will be useful in predicting long-term leach rates. Although nuclear waste glasses would be marginally durable in most commercial glass applications, the "normal" leach conditions in a repository present extremely low reaction rates, regardless of composition.

Leachant Flow Rate Effect

A large section of the chapter provides a general review of glass leaching in systems involving flow. The authors consider the effects of flow rate and contact time on leaching behavior in a system in which leachate solution is removed at a prescribed rate and replaced with leachant of the original composition. This procedure is called the pulse-flow method.

The effect of flow rate of the leachant on the leach rate is unequivocal, and this is recognized in the general glass-durability literature. It is obviously a result of the change in leachant composition as the glass reacts with the leachant.

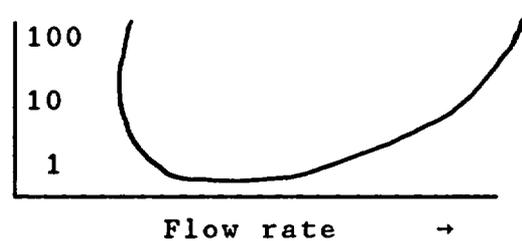
In quantitative terms, the leach rate is shown to depend directly on flow rate at "sufficiently" low flow rates; as flow rates increase, the leach rate becomes essentially constant and independent of flow rate. This is simply visualized as follows:



However, the picture is complicated by the fact that those glasses that reach a high equilibrium pH at low flow continue

to decompose quite readily at these low flow rates. A comparison of a relatively resistant glass, DWRG, with a less resistant glass, TDS-131, would indicate the following relative solubility with flow rate.

Ratio of leach
rates; $\frac{\text{DWRG}}{\text{TDS-131}}$



This highlights a "worst case scenario," where conditions alternate between slow flow and fast flow.

The authors have accumulated a substantial amount of data on flow rate. This data should permit the construction of a model. Validation of the model would then hinge upon further experiments in the laboratory and in the field.

Temperature Effect

As with commercial glasses, the activation energy for leaching is positive, so that the leach rate increases with temperature. The effect is lessened at slower flow rates as a result of near saturation.

There are several sets of data that should permit estimation of temperature coefficients. Models could be constructed and tested using these data.

Leachant Effect

The effect of leachate composition is fairly well documented over the range of "normal" repository conditions. It depends on pH and relative saturation with reactants such as silica and alumina. The role of competing ions is obviously important, but needs better definition. For the systems studied, it should be possible to construct simple models.

Protective Films

A most useful contribution of Chapter 1 is the recognition of the vital role of protective "films" coupled with the recognition that such a film is not the same as a silica-rich leached glass layer. However, no guidelines are offered for adjusting the glass composition to enhance the formation of protective layers. At least three concepts are articulated, all of which demand further study:

(1) Solid-state transformations are expected to control dissolution behavior under conditions of very slow flow, even at low temperatures.

(2) High-temperature studies can be used to predict low-temperature transformations.

(3) Iron tends to precipitate iron silicates. In some cases, this could increase solubility as silica is removed from the glass. In other cases, this could decrease reaction rates because of protective film formation.

Methodology and Data Validity

For the most part, the experimental approaches are reasonable but lack a coherent methodology. Additionally, it is not always clear as to what parameters are actually in effect for a given test.

The pulse-flow test is advanced as being most significant. A review of the procedure and a formal evaluation of it might have helped resolve questions such as the following:

Is leachate stratification really non-existent, as stated?

Does not the replenishment technique alter significantly the leachant composition?

The calculation of glass "grain" surface area is questionable. There is evidence to suggest that real areas are substantially larger (by as much as 2 times) than proposed by the authors. Further, there does not seem to be any account taken of the decrease in effective grain size as the test progresses. In the extreme, it decreases to the vanishing point. Thus, it is not clear whether some of the low leach rates computed are due to the reaction kinetics or to substantial dissolution of test material.

Repository Conditions

The work is predicated on "normal" repository conditions, defined as very low flow rates, pH between 7 and 9, and temperature in the 40-90°C range. The data and discussion affirm that nuclear waste glasses present no risk under these conditions.

The glass composition is not the controlling parameter for leaching in a repository. Rather, the repository is in control and the assumption made in this report is that "normal" will persist with no interruptions.

An important question is whether the repository will indeed remain normal. A worst-case scenario (involving events that might increase flow rate, introduce complexing ions, and defeat the moderating effect of silica saturation, or allow pH excursions above 9 or below 7) is not considered. Can flow rate increase? This worst case could involve a static condition interrupted suddenly by high flow.

If uninterrupted "normal" conditions can be guaranteed, then the study seems to be moving in the right direction, and in fact eventual conclusions are virtually self-evident. If "normal" conditions can be interrupted, the boundary conditions need to be defined and included.

Terms and Concepts

Some comments on terms and concepts in Chapter 1 are given below:

- "Exposure Time" and "contact time" really relate to flow rate, which in turn relates to saturation level.
- "Modification,...of glasses after leaching..." was written when what was meant was "glasses modified by leaching (p.1.2, par. 3).
- "Leach" is used to mean both selective attack (the classic definition) and also used to mean network, or total glass-structure destruction (conventionally called "etch"). Thus Q (p.1.3) really means total glass-corrosion quantity.
- "Characteristic alteration time" is not defined (p.1.4, par. 3).
- "The preferred representation of these glasses" (p.1.5, par. 5) does not indicate preferred by whom, and for what.
- "Classic Model" - This is referenced several times with the suggestion that nuclear waste glasses disobey the "classic model." Not so, they behave quite similarly to other low-durability glasses.
- Simply because data for nuclear waste glasses tend to agree with data for ancient glasses does not "validate conclusions based on short-term laboratory tests...." (p.1.55, par. 2).

Comments and Questions on Data and Materials

- Discrepancies do exceed ± 5 percent in some cases (p.1.5, par. 4 and p. 1.6, table 1.1).
- Concern remains about stratification in the leachate despite the authors' assurances (p.1.11, Fig. 1.2 and 1.13,1).

- Is the extrapolation to long contact times, using S/V as a scaling factor, substantiated? (p.1.11-1.12). See the discussion above on possible errors in the surface area calculation for powders (p.1.12, par. 1).
- The effective (i.e. real) surface area created as the test progresses is not discussed. Has it been considered? (p.1.12, par.1).
- The test procedure is unclear for data in Tables 1.2 and 1.3.
- How was H₂O⁺ determined? (Table 2)
- The validity of the pulse-flow test needs further evidence for confirmation, especially in relation to "replenishment" technique.
- The data points for 25 ml/h do not fit the curve (Fig. 1.4), nor do data fit in Fig. 1.20.
- How was iron redox state determined? (p.1.45)
- The solid-state transformation conclusions need more validation data (p.1.34) as does the use of high-temperature tests to predict crystalline species at low temperature (p.1.49 - 1.53).
- The importance of iron as a so-called major building block for crystalline species should be explored further (p.1.57, par. 2).

RELATED HLW REPORTS

Hench, L. L., "Physical Chemistry of Glass Surfaces." J. Non-Cryst Solids, 25: 343-369, 1977.

Plodinec, M. J., Jantzen, C. M., and Wicks, G. G., "A Thermodynamic Approach to Prediction of the Stability of Proposed Radwaste Glasses," in Nuclear Waste Management, Advances in Ceramics, Vol. 8, G.G. Wicks and W.A. Ross (editors), pp. 491-495. The American Ceramic Society, Columbus, OH.

Clark, D. E., Pantano, C. G., Jr., and Hench, L. L., Corrosion of Glass, Ashlee Publishing Company, New York, New York, 1979.

Jantzen, C. N. and Plodinec, M. J., "Thermodynamic Model of Natural and Nuclear Waste Glass Durability," J. Non-Crystalline Solids, 67, 207-223, 1984.

Paul, A., "Chemical Durability of Glasses; A Thermodynamic Approach," Journal of Materials Science, 12, 2246, 1977.

APPLICABILITY TO DATA TO LICENSING

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

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

Issues identified are 2.3.1 regarding physical, chemical and mechanical properties of the waste form with time, 2.3.2 regarding solubility of the waste form under repository conditions, and 2.3.2.1 regarding possible dissolution mechanisms of the waste form under repository conditions.

- (b) New Licensing Issues

- (c) General Comments for Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Pacific Northwest Laboratory Operated for the Department of Energy by the Battelle Memorial Institute, Columbus, OH.

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

Harker, A. B.
Mendel, J. E., Compiler
"Final Report of the Defense High-Level Waste Leaching Mechanisms Program, Chapter 2, Surface Layers in Leached Borosilicate Glass High-Level Defense Nuclear Waste Forms"
PNL-5157, August 1984. Available from NTIS.

DATE REVIEWED: 8/17/87; Revised 2/29/88.

KEY WORDS

Data analysis, literature review, microscopy, spectroscopy, visual examination, x-ray diffraction, laboratory, air, brine, deionized, simulated groundwater, ambient pressure, high pressure, high temperature, static (no flow), glass (defense waste reference glass), TDS-131, PNL 76-68, defense high-level waste (DHLW), matrix dissolution (glass), formation of alteration layers in glass.

TYPE OF DATA

(1) Scope of the Report

Extensive review of experimental data and data analyses relating to the chemical composition, morphology, and crystallinity of leached surface layers formed on borosilicate waste glasses by various types of leachants. Data obtained from contracting laboratories reports and other literature.

(2) Failure Mode or Phenomenon Studied

Growth of alteration layers in glass subject to leaching.
Alteration layer growth mechanism.
Alteration layer thickness and morphology.
Composition of alteration layers and other solid products.
Elemental leach depths.
Growth rates of leached surface films.

MATERIALS/COMPONENTS

Defense Waste Reference Glass (DWRG)
TDS-131 Glass
PNL-76-68

TEST CONDITIONS

(1) State of the Material being Tested

Glass monoliths and powders.

(2) Specimen Preparation

DWRG and TDS-131 glass surfaces were leach tested as-cast, polished with 3- μ diamond grit, thermally fractured, 600-grit polished, 360-grit polished, 400-grit polished, and with 600-grit scratches on 3- μ polish.

(3) Environment of the Material being Tested

IAEA Water Replacement Testing.
MCC-1 Static Leaching Testing.
Flowing Leachant Testing.
Water Exchange Testing.

Test Pressures: ambient and hydrothermal conditions.
Test Temperatures ($^{\circ}$ C): 20, 70, 90, 138, 160, 201, 225, 230, 247, and 250.
Exposed Surface Area to Solution Volume Ratio (SA/V, [m^{-1}]): 10 to 20, 20 to 50, 0.1, 10, 1.2×10^{-5} , 2300, 7, 360.
Test Time: 209 days, 14 days, 28 to 400 days, 6 months, 143 days, 1 to 2 years, 1800 h, 158 h, 102 h, 361 h.
Leachant Type: Highly Dilute Deionized Water, Grande Ronde-type Silicate Water, IAEA Deionized Water, Brine.
Leachant Flow Rate (cm^3/h), 0.5, 50.
Water Exchange Rates (volume %): 25% over 1 to 30 days.
Solution pH: 5.5, 11.4, 9.6, 10.6, 9.9, 12.4, 10.3 to 10.7.
Solution Eh: -3 mV.

Additional materials in the test environments: basalt, ductile iron, canister metal.

METHODS OF DATA COLLECTION/ANALYSIS

Scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDXS), secondary ion mass spectrometry (SIMS), x-ray photoelectron spectroscopy (XPS), chemical solution concentration analyses, sputter-induced photon-induced spectroscopy (SIPS), Auger electron spectroscopy (AES), scanning Auger spectroscopy (SAM), powder x-ray diffraction (XRD), optical microscopy.

AMOUNT OF DATA

There are seven tables.

Table 2.1--"Comparison of Calculated Elemental Leach Depths, from Solution and Gel Layer (EDXS) Concentration Data, with Those Observed by SEM/EDXS in a DWRG Alteration Region Produced in 183 Days of IAEA-Type Testing in Deionized Water at 90°C." Calculated Layer Thickness and SEM/EDXS-Based Layer Thickness, both in microns, are given for nine elements.

Table 2.2--"SEM/EDXS Comparison of Alteration Layer Thickness and Chemical Composition on 600-Grit-Polished DWRG Monoliths Exposed to Different Static Leaching Environments at the University of Florida. Atomic ratios were determined by quantitative EDXS using DWRG and pure phase nepheline reference standards, with the experimental uncertainty estimated at 10%." Composition data for six elements are given normalized with respect to Si for four different test cases.

Table 2.3--"Elemental Ratios observed by Quantitative EDXS in Alteration Layers Produced by 270 Days of Static Deionized Water MCC-1 Leach Testing at 90°C on Two Samples of the DWRG (estimated uncertainty 10%). Composition data for seven elements are given normalized with respect to Si for two different test cases.

Table 2.4--"Elemental Distributions Determined by EDXS in a 1-Micron Alteration Layer Separated from a Thermally Fractured Sample of the DWRG (Figure 2.2). MCC-1 leach conditions: 209 days in static deionized water at 90°C. Uncertainty of determinations estimated at 10%." The elemental composition for seven elements is given normalized to Si content for three layers: 0.0-0.5 micron, 0.5-1.0 micron, and the bulk glass.

Table 2.5--"Solid Reaction Products Observed in Dissolution Testing of the DWRG and TDS-131 Glass at 90°C (GND = groundwater, DI = deionized water)." The mineral phases and their nominal stoichiometry are given.

Table 2.6--"Crystalline Products Identified in Reaction of Glass and Water Under Hydrothermal Conditions." The temperature, time, grams of water, and crystalline phases are listed for 23 runs.

Table 2.7--"Disposition of elements in DWRG Upon Reaction with Water."

There are 34 figures.

Figure 2.1--"SEM Micrographs of the Alteration Layers Formed on 3-Micron-Grit-Polished DWRG in 28 Days of Deionized Water leaching at 90°C Under MCC-1 Conditions." Three micrographs are given, at 200x, 2000x, and 5000x magnification.

Figure 2.2--"Seven SEM Views of Two Alteration Layers Formed on a Sample of the As-Cast DWRG with a Thermal Fracture Surface. Leach conditions: 209 days, deionized water, 90°C, SA/V = 10 to 20 m⁻¹." The micrographs show Alteration Layers at 2000x, Outer Surface at 5000x, Bottom Surface of Outer Layer at 5000x, Upper Surface of Inner Alteration Layer at 5000x, Bottom Surface of Inner Alteration Layer at 2000x, Bottom Surface of Inner Alteration Layer at 5000x, and Leached Glass Surface Magnification at 2000x.

Figure 2.3--"Six Alteration Layers Formed on a Sample of TDS-131 Glass During Flow Test Leaching at the University of Florida. conditions: 50 cm³/h, deionized water, 90°C, 600 grit surface polish." The magnification is 2000x.

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Figure 2.5--"Plot of Calculated Alteration Layer Densities on Leached DWRG Surfaces as a Function of Flow Rate of Deionized and Simulated Groundwaters. The data were taken from water replacement test at Catholic University with effective flow rate calculated at a normalized SA/V x t value." Surface Layer Density in g/cm³ ranging from 0.5 to 2.5 is plotted versus Flow Rate in m/yr from 0 to 100. Data are given for deionized water at both 70°C and 90°C and for silicate water at 70°C.

Figure 2.6--"SEM Micrographs of the Alteration Layers Produced on Samples of the DWRG in 28 Days of MCC-1 Type Testing in Deionized Water at 90°C as a Function of Surface Finish." Three micrographs all at 2000x magnification show the effects of the use of 3 μ diamond, 600 grit powder, and 400 grit paper.

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Deionized Water, 28 days, 600 grit polish; Deionized Water, 143 days; Deionized Water + Canister Metal, 7 days.

Figure 2.8--"SEM Micrographs Demonstrating the Effects of precipitate Deposition on the Extent of Pitting of the DWRG Surface During Leaching. conditions: 7 days MCC-1 leaching at 90°C in deionized water with an equal surface area of the reference canister metal and DWRG." Four micrographs are given: Top Surface of DWRG at 2000x; Bottom Surface of DWRG at 2000x; Top Leached Glass Surface at 200x; Bottom Leached Glass Surface at 200x.

Figure 2.9--"SEM Comparison of Surface Precipitate Formation on the DWRG in Deionized Water at 90°C With and Without the Reference canister Metal Present After 143 Days of Static Leaching Under MCC-1 Conditions." Two micrographs are given.

Figure 2.10--"SEM Micrographs of the Precipitates Formed on the Reference Canister Metal in Deionized Water Leaching with the DWRG at 90°C After 143 Days." Two micrographs are given, one at 2000x and the other at 5000x magnification.

Figure 2.11--"Growth of the Alteration Zone on Samples of the DWRG as a Function of Time of Exposure to Deionized Water at 90°C Under MCC-1 Conditions (except where noted). Several conditions and surface finishes are represented. Open circles = TDS-131, 0.5 cm³/h flow DI water; closed circles = 3-micron polished samples of DWRG (MCC-1); squares = DWRG with 600-grit polish (MCC-1); diamonds = DWRG with 3-micron polish + an equal surface area of RCM (MCC-1); triangles = thermally cracked sample of as-cast DWRG (MCC-1). The arrows indicate that portions of the layers were significantly thicker; the dashed lines show the regions bound by the uncertainty in the measurements." Alteration layer thickness (microns) from 0 to 6 is plotted against days leached from 0 to 200.

Figure 2.12--"SIPS Depth Profiles for Polished DWRG After 100 H in Deionized Water at 90°C at SA/V = 0.1 m⁻¹. At the earliest stages, congruent dissolution of the DWRG depletes all elements except Si and B in the surface film." The intensity in photon counts per second from 10 to 10⁵ is plotted versus depth in μm from 0 to 0.3 for eight elements.

Figure 2.13--"SIPS Depth Profiles for Polished DWRG After 28 Days in Deionized Water at 90°C at SA/V = 0.1 m⁻¹. At this stage of dissolution the surface film shows the formation of a layer of hydrated Fe formed either by adsorption or precipitation." The intensity in photon counts per second from 10 to 10⁵ is plotted versus depth in μm from 0 to 0.4 for eight elements.

Figure 2.14--"SIMS Depth Profiles for Polished DWRG After 100 H in Deionized Water at 90°C at SA/V = 10 m⁻¹. Later in the dissolution process an outer layer is formed in the alteration zone as hydrated Mg and Mn precipitate or absorb at the water-glass interface." The intensity in photon counts per second from 10 to 10⁵ is plotted versus depth in μm from 0 to 0.6 for five elements.

Figure 2.15 A and B--"SIMS Depth Profiles for Polished TDS-131 Glass After 28 Days at 90°C in Deionized Water at SA/V = 10 m⁻¹. The profiles show the multiple layer structure of the elemental distribution in the alteration zone. Ca and Sr are enriched in the inner layer." In both figures intensity in counts per second from 1 to 100000 are plotted versus depth in μm from 0 to 4. Profiles for four elements are given in A and profiles for four other elements are given in B.

Figure 2.17--"EDXS Depth Profiles of the IAEA Leach-Tested Sample Shown in Figure 2.4." For eight elements, weight percent is plotted versus depth in microns (0 to 150.0). Weight percent scales vary for elements: 0 to 8 for Ca, Mi, and Al; 0 to 12 for Na; 0 to 16 for Mn and U; 0 to 40 for Si and Fe.

Figure 2.18--"XPS Spectra of the Fe 2p Electron Levels in the Bulk DWRG and in the Alteration Layers. The spectra show the Fe to be more oxidized in the leached layers." The spectra for the surface of the gel layer, the bottom of the gel layer, and the glass surface beneath the gel layer are given as amplitude plotted versus the binding energy (eV) from 750.0 to 700.0.

Figure 2.19--"XPS Spectra of the U 4f Electron Levels in the DWRG and UO₂. The comparison shows the DWRG to have U in the UO₂._x chemical state." The spectra for the bulk glass and the UO₂ are given as counts/100 (from 0 to 75.00) plotted versus the binding energy in eV (from 415.0 to 365.0).

Figure 2.20--"XPS Spectra of a Clean DWRG Surface and a Sample That Has Been Exposed to a High-SA/V Leach Solution for 2 Weeks at 90°C. The short exposure under near steady-state conditions has produced both leaching and precipitation reactions." The spectra are given in counts/100 (from 0 to 32 for the original surface and from 0 to 20 for the specimen after leaching) plotted versus the binding energy (eV) from 1095 to 95.

Figure 2.21--"SEM Micrograph of the Alteration Products Formed on a Sample of the DWRG After 6 Months of Static Leaching at 90°C in Deionized Water at a High SA/V."

Figure 2.22--"SEM Micrographs and EDXS Spectrum of Analcime Formed in the 90°C Deionized Water Leaching of the DWRG at High SA/V. A similar analcime type formed in TDS-131 glass leaching has a factor of 10 higher Cs content." The spectrum has no units but does give the stoichiometry of the analcime; there are two micrographs.

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Figure 2.25--"SEM Micrograph and EDXS Spectrum of a Hydrated Aluminum Containing Product Formed in Near-Steady-State Deionized Water Leaching of the DWRG at 90°C and High SA/V (as in Figure 2.20)."

Figure 2.26--"SEM Micrograph and EDXS Spectrum of a Hydrated Silica Precipitate Observed in Silicate Water Leaching of the DWRG at 90°C and an SA/V of 360 m^{-1} ."

Figure 2.27--"SEM Micrograph, EDXS Spectrum, and XRD Pattern of the Mixed Magnesium Oxychloride $[\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O} - \text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot \text{H}_2\text{O}]$ Preferentially Formed on the Surface of the DWRG in MCC-Static Leaching in Brine at 90°C for 28 Days."

Figure 2.28--"Plot of the Experimental Runs and the REaction REsults as Sketches of the Surface of the Glass Samples, Approximately as Viewed at 50x. In the lower portion of the figure, no crystalline phases were observed; scratches were enhanced by the reaction. In the upper portion of the figure, crystalline reaction products are common and their abundance and morphology are indicated." Temperature is plotted both as °C (from 50 to 250) and as $1000/T$ in kelvins (from 2.75 to 2.00) versus the log t in h (from 1.25 to 3.5).

Figure 2.29--"EDXS Trace and SEM Micrographs of Analcime Crystals. Upper right, analcime crystals with calcium silicate spheres, run 3-C (201°C, 1800 h). Scale bars 50 microns.)"

Figure 2.30--"EDXS Trace and SEM Micrographs of Weeksite Clusters. Left, tapered weeksite crystals over an analcime crystal, calcium silicate sphere (see Figure 2.34) to top right, run 3-C (201°C, 158 h). Right, (run 20-F, 230°C, 1800 h) bluntly terminated blades of weeksite; in the background

are analcime, calcium silicate (Figure 2.31) and two forms of silica. (See Figure 2.34 right top and bottom). Scale bars 100 microns."

Figure 2.31--"EDXS Trace and SEM Micrographs of Calcium Silicate Crystals from run 20-F (230°C, 1800 h). Additional phase in right-hand panel is silica. Scale bars 25 microns."

Figure 2.32--"EDXS Trace and SEM Micrographs of Fibrous Calcium silicate Phase (run 21-D, 225°C, 361 h). The shorter, brighter, feathery phase is wecksite. The disks are analcime crystals which were trapped between the glass slice and gold capsule when they grew. Scale bars 50 microns."

Figure 2.33--"SEM Micrographs of Crystalline Calcium silicates. The EDXS trace would be the same as Figure 2.32 except for the lack of SR. (A), run 21-D (225°C, 361 h). In (B) there are two morphologies present which give the same EDXS trace (run 3-D, 247°C, 102 h)."

Figure 2.34--"EDXS Trace and SEM Micrographs of "Silica" Phases. Stout prisms (left): this morphology resembles that of quartz (SiO_2) although DCP/AES analysis shows the presence of Li and B in addition to Si, run 20-C (230°C, 1800 h). Laths (bottom right): the individual crystals resemble those figured by Savage (1981), although the organization in the cluster is different (run 20-F, 230°C, 1800 h). Ragged cluster (top right): sphere in background is calcium silicate (see Figure 2.33 A), run 21-D (225°C, 361 h). Scale bars 25 microns."

UNCERTAINTIES IN DATA

The uncertainties in the data are not discussed in the review and the original references must be applied to for that information.

DEFICIENCIES/LIMITATION IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

"The sharp boundary between the alteration layers and the bulk glass, the marked chemical distributions within the alteration layers, and the well-defined physical features of the alteration region indicate that its properties are directly affected by reactions with the aqueous environment and are not simply the result of incongruent dissolution of the glass matrix."

"The presence of metallic Fe in oxygenated leaching environments accelerates the dissolution process through iron-silicate reactions, producing alteration layers dominated by Fe chemistry."

COMMENTS OF REVIEWER

This report provides information on the physical and chemical properties of leached glasses. A physical picture of the alteration layers produced by leaching of the glass waste form is as follows. The contact of water with the glass surface initiates the formation of the alteration layer. This occurs by leaching away the soluble cations, leaving a skeletal structure of the original form which retains the initial geometrical dimensions. The growth of the alteration layer proceeds into the glass with cracks and microscale roughness accelerating the process as much as an order of magnitude. Pit formation in the altered glass surface is common with pits preferentially appearing on stress lines and in areas of surface disruption. Polished or smooth fractured surfaces produce alteration layers with distinct layering; roughened or poorly polished surfaces form alteration layers that are highly convoluted. In all cases (except when they slough off) the alteration layers have good integrity and a well-defined boundary with the bulk glass.

Surface layers on the leached glass include crystalline deposits imbedded in an amorphous precipitate. This material is in contact with the generally amorphous altered layer. The interface between the altered layer and the bulk glass is physically and chemically well defined except for a reaction zone, generally less than 1 micrometer thick, which exhibits extensive pitting and is depleted in the more soluble elements (B, Li, Na). The properties of the altered layer are influenced by reactions with the aqueous environment and are not due to diffusion effects. Dilute leachants produce thick low-density layers while concentrated leachants produce thin high-density surface layers.

Additional leaching experiments conducted under hydrothermal conditions at temperatures as high as 250°C accelerated the dissolution-crystallization process but produced products identical to those formed at lower temperatures. This indicates that the precipitation reactions do not change significantly over this temperature range.

The presence of reactive solids, such as canister metal or ductile iron in the leach system with initially air-saturated deionized water, significantly accelerates the removal of silica from the glass and leads to the formation of colloidal complexes and well-defined crystalline precipitates on the

surface. Small node-like and flocculent precipitates are common in all systems where water flow is low enough for saturation to occur. This may indicate that crystallization on the altered layer is occurring. However, in deoxygenated deionized water the reaction is much less aggressive which indicates the importance of the Eh in this case.

In summary, the report has provided a great deal of information concerning the physical and chemical nature of the altered layer including its chemical composition, the distribution of elements within it, the composition and nature of crystalline deposits formed on the surface and its rate of formation under several specific leaching conditions.

In spite of this valuable information, the most important aspect of the leach mechanism is that the alteration layer is more a product of the leachate concentration than of any property of the glass. Might not the fact that thick alteration layers are found in high leach rate, dilute leachate environments and thin alteration layers are found in low leach rate, concentrated leachate environments suggest that it plays only a minor role in glass leaching?

APPLICABILITY OF DATA TO LICENSING

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

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

Related to ISTP issue, 2.3.2.1.1, which waste form dissolution mechanism or mechanisms are most likely?

- (b) New Licensing Issues
- (c) General Comments on Licensing

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.

(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. Available from NTIS.

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 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/m² (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 cm⁻¹, (b) Stripa Groundwater with SA/V = 1.0 cm⁻¹, and (c) Deionized Water with SA/V = 0.1 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 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 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.

CONCLUSIONS OF AUTHOR

"In comparison to pure water, the rates of leaching for 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 reduces the driving force for glass dissolution."

"The relative leach behavior of various waste glasses has been found to be the same in these field tests as in the laboratory tests."

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 the Battelle Memorial Institute, Columbus, OH.

(b) Author(s) References, Reference Availability

White, W. B., Pantano, C. G., Apted, M. J. and
McVay, G. L.
Mendel, J. E., Compiler
"Final Report of the Defense High Level Waste Leaching
Mechanisms Program, Chapter 4, "Dissolution of Specific
Radionuclides"
PNL-5157, August 1984. Available from NTIS.

DATE REVIEWED: 6-15-89

PURPOSE

"Technetium, uranium and the transuranic elements, with their long half lives, are the major radionuclides from the waste that survive well into the 'geological' time period of the repository." Those are elements of greatest significance to the long-term safety of a defense nuclear waste repository." "The sections that follow discuss experimental results on the dissolution of these elements from the MCC reference glass."

KEY WORDS

Data analysis, experimental data, theory, supporting data, general corrosion, leaching, solubility, RBS, Eh (platinum electrode), corrosion, SIMS, laboratory, basalt composition, brine, deionized, groundwater, tuff composition, Fe, acidic solution (pH <7), basic (alkaline) solution (pH >7), redox condition, glass (defense waste reference glass), glass (PNL 76-68) leaching, matrix dissolution, technetium release, uranium release, actinide release, iron release, iron effect.

CONTENTS

Text: 55 pages, 52 figures, 7 tables, and 41 reference.

AMOUNT OF DATA

There are 52 figures and 7 tables. The first 6 figures are for the purpose of explaining redox principles and are apparently taken from other publications.

Figures 4.7 to 4.20 involve DWRG glass that has been doped with technetium. Figures 4.7 to 4.11 show extraction data for technetium at pH 1, 3, 7 and 11, at temperatures of 40, 70 and 90°C for periods up to 55 days. Figures 12 through 16 show data on the dissolution of the parent glass at 90°C after 55 days (leach data for glass components at pH 1 and SIMS profiles after reaction in water). Data in Figures 4.17 to 4.21 are for reduced and oxidized systems involving pH 1, 3, 7, and 11 at 70°C for 60 days.

Uranium extraction data for DWRG glass are shown in Figures 4.22 through 4.25; the release of uranium "normalized" to boron is recorded for pH 1, 3, 7, and 11 at 90°C up to 30 days.

Extraction of iron plus some alkali elements, apparently from DRWG glass is shown in Figures 4.26 through 4.28 for tests at pH 1, up to 30 days at 40°C, 70°C and 90°C.

Neptunium-237 doped DWRG glass was used for generating the data in Figures 4.29 through 4.31. Boron, silicon and sodium release up to 55 days at 90°C are shown for deionized, tuff and basalt waters with and without iron present.

The effect of dissolved silica in silicic acid solutions, as well as in actual groundwater, is shown in Figure 4.32; the extraction of boron from DWRG glass up to 28 days is presented.

Iron effects are shown in Figures 4.33 through 4.36. The release of Si and Ca from DWRG glass for periods up to 28 days when exposed to basalt and tuff waters containing iron at 90°C are shown in Figures 4.33 and 4.34. Figure 4.35 shows similar data for PNL 76-68 glass and Figure 4.36 depicts SEM photos of the PNL 76-68 surfaces after test completion.

The release of neptunium-237 from DWRG glass (Np doped) is shown in Figures 4.37, a & b, through 4.39, a & b, for deionized water, basalt water and brine at 90°C up to 57 days, with and without iron present.

Figures 4.40, a & b, through 4.42, a & b, show data for release of plutonium-239 from DWRG glass (Pu doped) under the same conditions as above for neptunium-237.

Figures 4.43, a & b, through 4.46, a & b, show data for uranium released from the Np- and Pu-doped glasses under the conditions shown in Figures 4.37-4.42 (with the exception of DI water).

Rutherford backscattering spectra of glass surfaces are shown in Figures 4.47 through 4.51. They give C, O, Si, Al, Fe and U which remain in DWRG glass after leaching up to 56 days in deionized water at 90°C (Figure 4.47) and after leaching 28 days with and without iron in the water Figure 4.48). Also shown is Pu and the total concentration of Nd+Ce+La+Pu in Pu-doped PNL 76-68 glass after exposure to brine and deionized water, with and without iron (Figures 4.49 and 4.50).

The solubilities of Pu and Np as they originate from DWRG glass versus the solubilities as they originate from the hydrated oxide compounds are compared at pH 0.5 to 9.5 in Figures 4.51 and 4.52. The solubilities depend on the origins of solid phases since the soluble species can be different.

Table 4.1 shows the values of SA/V [Ed. surface area/volume] that were calculated for the experiments involving a technetium-doped glass (sec. 4.3).

Table 4.2 lists the starting and ending pH values for solutions used in the leaching experiments with technetium-doped glass (sec 4.3).

Table 4.3 lists the starting and ending pH values for solutions used in the leaching experiments where uranium was determined (sec 4.4).

Table 4.4 shows the composition of tuff, basalt and brine waters used in the leaching experiments where the extraction of neptunium, plutonium and uranium was measured from doped-DWRG glass with and without iron present sec. 4.5.

Tables 4.5-4.7 show respectively the distributions of Np, Pu and U in colloidal form, in solution, on the iron coupon and on the reaction vessel walls after the 56 day test at 90°C in brine, basalt and DI water with and without iron (sec. 4 5 experiments).

TEST CONDITIONS

Crushed glass samples sized from 0.35 to 0.70 mm in the one case specified) were reacted under static conditions that included pH from 1 to 11, temperature from 40°C to 90°C and times up to 75 days. Leach solutions included HCl and NH₄OH as well as DI water, basalt water, tuff ground water and salt brine. Nominal SA/V was found to be 10 m⁻¹. Redox potential was not directly measured in the experiments which are the

principal subject of this report; the control of redox was however discussed in an introductory section. Control of oxidation conditions was accomplished by conducting the experiments in atmosphere-specific closed capsules or by defining pH. To determine the effect of iron ions, ductile iron coupons were immersed in the leachants.

Materials studied were principally DWRG glasses that had been doped with technetium, uranium, neptunium and/or plutonium. PNL 76-68 glass was used in some experiments relating to leaching of parent glass components and the effect of iron. The specific glass compositions were not given.

UNCERTAINTIES IN DATA

With respect to the data for the technetium-doped glass (sec 4.3), the following comments were made: (1) "the error in counting statistics is about equal to the size of the symbols on the graphs" and (2) error bars for the range of Eh are shown in Figure 4.17.

With respect to the data for the extraction of uranium (sec. 4.4), there are comments regarding the drift and difficulty of control of pH.

With respect to the data for the Np, Pu, U doped glass experiments sec 4.5 numerical ranges are shown for the total amount of Np, Pu and U calculated as shown in Tables 4.5 to 4.7. Error bars are also given for the boron release plotted in Figure 4.32.

DEFICIENCIES/LIMITATIONS IN DATABASE

Section 4.5 notes that (1) "a detailed chemical analysis of filterable material and of the iron surface may be required to" determine whether the uranium is precipitating on the iron coupon, and is being subsequently released as iron is corroded, or whether it results from a decrease in redox potential in the presence of iron, (2) "obtaining a clear analogy in release behavior... is further complicated by the fact that reactions are obviously continuing", and (3) empirical correlation of chemical similarity... may be fortuitous and should be confirmed...".

There is further comment that there are (1) "several cautionary aspects..." that "...complicate any attempt to reliably use radionuclide solubility data to predict actual steady-state concentrations of radionuclides released from glass waste forms" and (2) "direct tests on glass waste forms" should be done.

There are several cautionary aspects regarding the assumption that steady-state radionuclide concentration observed in long-term tests on glass waste forms will correspond directly to measured solubilities of radionuclide-bearing solids. The first is that the actual radionuclides-bearing solids that form upon alteration of glass are typically not simple oxide and or hydroxides used in solubility studies. The second is that the steady-state concentration may be due to a state of dynamic balance between the kinetics of dissolution and precipitation, for solid components, and it is not due to a true thermodynamic equilibrium. The third is that the thermodynamics data are typically obtained from the solutions, which are quite different from the groundwater and may contain both increased concentrations and number of ionic species.

CONCLUSIONS OF AUTHOR

The conclusions drawn from the summary and the content are as follows:

"The dissolution behavior of technetium, uranium, neptunium and plutonium from defense waste reference glass was studied. The effect of Eh on the leaching behavior of technetium was found to be significant because the valence states have different solubilities." However, "the equilibrium redox conditions were found to pertain only at the extreme upper and lower ends of the Eh, that is, near the upper and lower stability limits of water."

"The dissolution of Tc from the waste glass under oxidizing conditions followed a mixed linear-parabolic kinetics and was strongly influenced by the initial pH of the solution. Dissolution of Tc was slowed by several orders of magnitude under highly reducing conditions."

"The form of the transuranic leached from waste glass was found to be at least partially associated with colloidal-sized particles (held on a 1.8 nm filter) in almost all tests. With deionized water leachant, the leached transuranic were almost totally filtered out; but with brine leachants the transuranic passed through the filter, showing that soluble species were dominant. Simulated groundwater leachants tended to exhibit an intermediate behavior."

COMMENTS OF REVIEWER

The summary does not seem to completely reflect the material content, neither in terms of scope of experiments reported nor in terms of conclusions reached. e.g. The effect of iron, which is the focus of much of the experimental work, is not mentioned in the "summary" although there is considerable experimental work and commentary, nor is there any statement

in the summary such as the one in section 4.1 to the effect that "The extent to which these effects can be described quantitatively and incorporated into rate equations is still open."

Regarding the effect of iron, a mechanism was described to show how the increased dissolution occurred. The iron present oxidizes to the ferrous ion which reacts with silica in solution to produce a precipitate of ferrous silicate. This precipitation leaves the solution undersaturated in silica and results in an increase in further glass dissolution.

The experimental data is contained in sections 4.3, 4.4 and 4.5. It is often difficult to understand the variables associated with the data, since it appears that they derive from different experiments that sometimes have very little in common. It appears that the base glasses used for the experiments were either DWRG or PNL 76-68, although this is not clear, and the specific compositions are not available in the body of the report. For instance, (1) the glass size was 0.35 ~ 0.70 μm in one case and -100 mesh in another case, (2) tests on Tc was performed at SA/V = 0.29 and 0.47 m^{-1} while other actinides was tested at SA/V = 10 m^{-1} , and (3) the majority of the test durations were 60 days while 75 days' tests were also used.

In the course of review, some specific comments regarding experimental conditions or assumptions arose as indicated below:

(1) Re: the assumption (Table 4.1) that crushed glass grains are spherical and that the surface area can be calculated on this basis... This reviewer notes that such grains are not spherical; they generally present as much as 2X the surface presented by a sphere of the same mesh.

(2) Re: the attribution of the decrease of Tc reaction rates with time to a "diffusive barrier layer" (p. 4.9) as shown in Figures 4.8-4.10... This reviewer notes at least three other causes: the change in pH (documented in table 4.2), the change in surface area of crushed glass as it is corroded away, and the diminishment of available Tc until it is close to the vanishing point.

(3) Re: the data in section 4.3 with respect to U extraction which is "normalized" to boron extraction rates... This reviewer notes that such a statement seems to imply some fundamental reaction phenomenon of which he is unaware.

(4) Many of the rate changes shown in data for U in section 4.4 may also be due to the causes cited above in item 2.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.2, 2.3.2.1, 2.3.2.1.1, 2.3.2.1.2, 2.3.2.3; All relate to dissolution and radionuclide release from the waste form.

(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 the Battelle Memorial Institute, Columbus, OH.

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

Apted, M. J. and McVay, G. L.
Mendel, J. E., Compiler
"Final Report of the Defense High Level Waste Leaching Mechanisms Program, Chapter 5, Radiation Effects."
PNL-5157, August 1984. Available from NTIS.

DATE REVIEWED: 9/30/87; Revised 4/26/88.

KEY WORDS

Literature review, brine, basalt composition, granite composition, tuff composition, salt, Cl, Br⁻, SO₄³⁻, basalt, granite, tuff, alpha radiation field, gamma radiation field, redox condition, commercial high level waste (CHLW), defense high level waste (DHLW), Pu, groundwater, corrosion (general), leaching (radiation enhancement), radiation effects.

TYPE OF DATA

Literature review includes data on the effects of alpha, beta and gamma radiation on structural damage to nuclear waste forms, and subsequent leaching performance of such irradiated waste form, are meager. Measurable structural damage begins at a cumulative dose of about 1×10^{23} alpha decays/m³ and "saturates" at a dose of approximately 5×10^{24} alpha decays/m³. These doses correspond to cumulative doses expected for commercial glasses within the first 10,000 y of disposal in a geologic repository. A rough correlation between degree of structural damage, as measured by percent increase in solid volume, and enhancement of initial leach rate has been established for irradiated nuclear waste forms. Ground waters exposed to radiation from nuclear waste forms will form free radicals, ionic, and molecular species that can significantly alter the geochemical environment in repositories. Gamma radiolysis effects, alpha radiolysis effects, reactions between radiolytically produced species and dissolved chemical species, presence of dissolved gases and interactive effects of solids including waste forms, metallic barriers, and host rocks. Study on the effect of radiation damage on potential repositories have focused on salt. Two

aspects of radiation damage in NaCl were discussed: colloid sodium formation and stored energy. The status of the computer codes that have been developed, to predict concentration of radiolytically produced species in simple ground water system was discussed briefly.

MATERIALS/COMPONENTS

Borosilicate glass, NaCl, Na₂SO₄, salt brine, tuff, basalt, granite, groundwater, synroc-c

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

Actinide-Doping technique, external heavy-ion and neutron irradiations

AMOUNT OF DATA

Tables

- 5.1 Primary radiolytic species G values for Gamma and 5MeV alpha radiation.
- 5.2 Gamma radiolysis of basalt ground water with methane.
- 5.3 Gamma radiolysis of basalt ground water without dissolved methane.
- 5.4 Results of alpha radiolysis on a cycle 4 synthetic permian brine using ²⁴⁴Cm.
- 5.5 Summary of total Pu release in MCC DWRG at 40°C in DI water.
- 5.6 Summary of pH change in MCC DWRG at 40°C in DI water.
- 5.7 Summary of Si release in MCC DRWG 40°C in DI water.
- 5.8 Reaction scheme for irradiated salt.

Figures

- 5.1 Expected volume changes as a function of dose and correlated to the waste storage times of both defense and commercial high-level waste forms. Dose range: 10²¹-10²⁷, swelling range: (-1)-(+6)%.

- 5.2 Increase in relative leaching L/L_0 versus volume change, for percent volume change from 0 to 40% and increasing leaching factor from 0 to 80.
- 5.3 Total gas pressures generated by salt solutions in a ^{60}Co irradiation field. Normalized dose range: 0-25 grad, pressure range: 0-100 ATM.
- 5.4 The effect of SO_4^{2-} on the total gas pressures generated by ^{60}Co irradiated field. Normalized dose range: 0-25 Grad, Pressure Range: 0-100 ATM.
- 5.5 Total gas pressures generated by brine and solid waste package components in a ^{60}Co irradiated field. Normalized dose range: 0-25 Grad, Pressure Range: 0-100 ATM.
- 5.6 Increase in elemental leach rates of MCC 76-68 waste glass as a function of gamma-dose rate at 70°C . Dose rate range: 0-2 MR/h elemental leach rates: 0-4 gr./m².h ($\times 10^3$).
- 5.7 Increase in pH due to dissolved irradiated salt as a function of integrated gamma dose to the salt. pH range: 0-14, pe range: (-12)-(+24), dose range: 5.7×10^4 - 2.3×10^5 R.
- 5.8 Effect of gamma radiolysis in acidity (pH) and oxidation potential (pe) on salt brine.
- 5.9 Plot of the concentrations of radiolytically produced species versus time as predicted by Radiol at a dose rate of 3.5 MRads/hr and initial oxygen concentration of 1.5 ppm. Time scale: 10^{-2} - 10^4 , concentration scale: 10^{-6} - 10^4 micromolar.

UNCERTAINTIES IN DATA

Uncertainties in many rate constants for radiation yields used in the computer modeling of radiolysis calculations and the lack of many appropriate rate constants are major limitations to the current computational efforts at modeling radiolysis of complex ground water.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF REVIEWER

"Measurable density change in waste glass begins at a cumulative dose of about 1×10^{23} alpha decays/m³ and

saturation at a dose of approximately 5×10^{24} alpha/m³. Leach rates increase by less than a factor of three even in waste glass with a saturated radiation dose. Radiolysis of repository fluids can yield a complex spectrum of products, including, in addition to the normal radiolytic products of water, oxalic and nitric acids from radiolysis of CO₂ and dissolved N₂, oxidizing chlorine species from radiolysis of Cl⁻, and high molecular weight organic compounds from radiolysis of methane. The radiolytic products enhanced the leach rate of plutonium by about a factor of two."

COMMENTS OF REVIEWER

The effect of radiation on the structural damage of nuclear waste forms is very important. Most studies on leaching of nuclear waste forms have been conducted with water in the absence of both a radiation field and other waste package barrier materials.

In this report there is information about the radiation damage of the waste form and the host rock and about the radiolysis of ground water solution. The section on the radiation damage reviews the current literature on these effects. The section on radiolysis presents and discusses new experimental data generated for ground water and ground water plus borosilicate glass.

Measurable structural damage begins at a cumulative dose of about 1×10^{23} alpha decays/m³ and "saturates" at a dose of approximately 5×10^{24} alpha decays/m³. These doses correspond to cumulative doses expected for commercial glasses within the first 10,000 years of disposal in a geologic repository. A rough correlation between degree of structural damage, as measured by percent increase in solid volume, and enhancement of initial leach rate has been established for irradiated nuclear waste forms.

The studies on the effect of radiation damage on potential repositories have focused on salt. Two aspects of radiation damage in NaCl that have received the most attention are colloid Sodium formation and stored energy.

Computer codes have been developed, and are being continually improved, to predict concentration of radiolytical produced species in simple ground water systems.

This excellent work is only the beginning in the understanding of the actual repository condition. More work is needed to understand the effects of radiation on radionuclide release rate from the waste form in the presence of radiation field and appropriate barrier materials.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

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

2.2.4.2.1 concerning the predicted rate of radiolytic generation of hydrogen, oxygen and other species due to gamma radiation in the vicinity of the waste package container.

(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.

(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 desorption, phenomenological model, Quarts, 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 nth 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 Apter, 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 Wick. 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 (Wick,

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

Pacific Northwest Laboratories operated for the Department of Energy by Battelle Memorial Institute, Columbus, OH.

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

Jackson, D. D.
Mendel, J. E., Compiler
"Final Report of the Defense High-Level Waste Leaching Mechanisms Program, Chapter 7, PROTOCOL, a Numerical Simulator for Glass Dissolution"
PNL-5157, August 1984. Available from NTIS.

DATE REVIEWED: 9/18/87; Revised 10/1/87.

KEY WORDS

Theory, leaching, PROTOCOL, leaching (radiation enhancement).

TYPE OF DATA

- (1) Description of computer software available via time sharing with Lawrence Livermore National Laboratory
- (2) Aqueous leaching.

MATERIALS/COMPONENTS

Glass of all types and other solids.
Na₂O, CaO, SrO, Cs₂O, Li₂O, Al₂O₃, DWRG glass, Fe₂O₃, UO₃, B₂O₃, Deionized water, Groundwater SiO₂, H₄SiO₄, Mg(OH)₂, SRL Glasses, TDS-131 Glass, MCC Reference Glass.

TEST CONDITIONS

General-purpose numerical simulator for the dissolution reactions of solids with aqueous solutions.

METHODS OF DATA COLLECTION/ANALYSIS

A complete description of the methodology embodied in PROTOCOL, i.e., the theory underlying the calculations that PROTOCOL does, is not given in Chapter 7. The essential information may be given elsewhere although no references are given in this chapter.

AMOUNT OF DATA

No original experimental data. Thirty-five figures and eight tables show PROTOCOL output. This output illustrates PROTOCOL capabilities, but is of no independent scientific interest.

Figures

- 7.1 PROTOCOL Files, and their use as a fortran code logic instructions and data.
- 7.2 Preprocessor files, a supporting set of preprocessor and data files.
- 7.3 Dissolution rates for amorphous silica at 298K; Aqueous species not removed. Concentration range: 10^{-5} - 10^{-2} molality; rate scale: 10^{-14} - 10^{-12} moles/sec.
- 7.4 Computed aqueous silica concentrations as a function of temperature. Amorphous silica in contact with static water at pH=6. Time scale: 10^{-3} - 10^0 y; silica concentration range: 10^{-5} - 10^{-2} molality.
- 7.5 Computed changes in dissolved silica concentrations as a function of flow rate. Amorphous silica at 313°K and pH=6. Time scale: 10^{-3} - 10^{-1} y; flow rates: 0.1-1 ml/d; change in concentration: 10^{-7} - 10^{-2} molality.
- 7.6 Computed effects of surface area on dissolved silica concentrations. Amorphous silica in static water at 313°K and pH=6. Time scale: 10^{-4} - 10^{-1} y; surface area: 0.1-10m²/g; silica concentration range: 10^{-4} - 10^{-2} molality.
- 7.7 Computed effects of initial silica concentration on dissolved concentrations. Amorphous silica in static water at 313°K and pH=6. Time scale: 10^{-5} - 10^{-3} y; Initial concentration: 10^{-20} - 10^{-4} molality; dissolved silica range: 10^{-5} - 10^{-3} molality.
- 7.8 Computed effects of changes in stability of H₄SiO₄ on time to saturate. Amorphous silica in static water at 313°K and pH=6. Time scale: 0-1 y; decrease from actual free energy range: -2500-0 J/mole.
- 7.9 Solubility of silica at 298K as a silicated component versus assigned log K for reaction $1:\text{SiO}_2(\text{OH})_2^{-2}(\text{aq}) + 2\text{H}^+(\text{aq}) = \text{SiO}_2(\text{sol}) + \text{H}_2\text{O}$ concentration range: $10^{-1.5}$ - $10^{3.5}$ molality; log K range: 24-27.

- 7.10 Estimated stabilities of alkali and alkaline-earth components versus pH. Free energy of formation range: 770-(-)620 kJ/mole pH range: 5-12.
- 7.11 Estimated stability of component silica. pH range: 5-12; free energy of formation range: -920-(-)800 kJ/mole.
- 7.12 Estimated stability of component B_2O_3 . Free energy of formation range: -1300-(-1210) kJ/mole for pH range: 5-12.
- 7.13 Estimated stability of component Al_2O_3 . Free energy of formation range: -1720-(-1600) kJ/mole for pH range: 8-12.
- 7.14 Estimated stabilities of alkali and alkaline-earth components versus S/V. Free energy of formation range: -770-(-620) kJ/mole for S/V range: 0-2000.
- 7.15 Estimated stability of component silica versus S/V. Free energy of formation range: -920-(-800) kJ/mole and S/V range: 0-2000.
- 7.16 Estimated stability of component B_2O_3 versus S/V. Free energy of formation range: -1300-(-)1210 kJ/mole and S/V range: 0-2000.
- 7.17 Estimated stability of component Al_2O_3 versus S/V. Free energy of formation range: -1720-(-)1600 kJ/mole and S/V range: 0-2000.
- 7.18 Estimated stabilities of alkali and alkaline-earth components versus residence time. Free energy of formation range: -770-(-)620 kJ/mole and residence time range: 0-250 d.
- 7.19 Estimated stability of component silica versus residence time. Free energy of formation range: -920-(-)800 kJ/mole and residence time range: 0-250 d.
- 7.20 Estimated stability of component B_2O_3 versus residence time. Free energy of formation range: -1300-(-)1210 kJ mole and residence time range: 0-250 d.
- 7.21 Estimated stability of component Al_2O_3 versus residence time. Free energy of formation range: -1720-(-)1600 kJ/mole and residence time range: 0-250 d.
- 7.22 Estimated free energies of formation for oxide components of leached residues from DWRG glass. Deionized water

leachant at 373°K. Free energy of formation range: -770-(-)650 kJ/mole and pH range: 9-10.5.

- 7.23 Estimated free energies of formation for silica in leached residues from DWRG glass. Deionized water leachant at 373°K. Free energy of formation range: -920-(-)800 kJ/mole and pH range: 9-10.5.
- 7.24 Estimated free energies of formation for boron oxide in leached residues from DWRG glass. Deionized water leachant at 373°K. Free energy of formation range: -1200-(-)1320 kJ/mole and pH range: 9-10.5.
- 7.25 Estimated free energies of formation for alumina in leached residues from DWRG glass. Deionized water leachant at 373°K. Free energy of formation range: -1750-(-)1630 kJ/mole and pH range: 9-10.5.
- 7.26 Estimated free energies of formation for iron oxide in leached residues from DWRG glass. Deionized water leachant at 373°K. Free energy of formation range: -720-(-)600 kJ/mole and pH range: 9-10.5.
- 7.27 Estimated free energies of formation for uranium oxide in leached residues from DWRG glass. Deionized water leachant at 373°K. Free energy of formation range: -1180-(-)1060 kJ/mole and pH range: 9-10.5.
- 7.28 Estimated free energies of formation of oxide components of leached residues from DWRG glass. Deionized and ground water leachant at 373°K. Free energy of formation range: -770-(-)650 kJ/mole and pH range: 9-11.5.
- 7.29 Estimated free energies of formation for silica in leached residues from DWRG glass. Deionized and ground water leachant at 373°K. Free energy of formation range: -920-(-) 800 kJ/mole and pH range: 9-11.5.
- 7.30 Estimated free energies of formation for boron oxide in leached residues from DWRG glass. Deionized and ground water leachant at 373°K. Free energy of formation range: -1200-(-)1320 kJ/mole and pH range: 9-11.5.
- 7.31 Estimated free energies of formation for alumina in leached residues from DWRG glass. Deionized and ground water leachant at 373°K. Free energy of formation range: -1750-(-)1630 kJ/mole and pH range: 9-11.5.

- 7.32 Estimated free energies of formation for iron oxide in leached residues from DWRG. Deionized and ground water leachant at 373°K. Free energy of formation range: -720-(-)600 kJ/mole and pH range: 9-11.5.
- 7.33 Estimated free energies of formation for uranium oxide in leached residues from DWRG glass. Deionized and ground water leachant at 373°K. Free energy of formation range: -1180-(-)1060 kJ/mole and pH range: 9-11.5.
- 7.34 Estimated steady-state releases of species from DWRG surface phase. Flow = 10 ml/d, T = 373EK, Time Range: 10^{-1} - 10^4 d, and the total moles of species released to outflow in range: 10^{-9} - 10^1 .
- 7.35 Estimated steady-state releases of species from DWRG surface phase. Flow = 10ml/d, T = 373°K, Time range: 10^{-1} - 10^4 d, and the total moles of species released to outflow in range: 10^{-9} - 10^1 .

Tables

- 7.1 Estimated stabilities of Montmorillonite. Standard free energy of formation at 298°K that was made by Tardy and Garrels and by PROTOCOL simulation.
- 7.2 Estimated free energies of formation of silicated component oxides in residues from leached TDS-131 glass at T=343K, kJ/mole. Compared with pure phases and components of layers silicates. pH range; 8.95-11.24.
- 7.3 Estimated free energies of formation at 373°K for oxide components of leached residues from DWRG glass, kJ/mole.
- 7.4 Estimated free energies of formation at 373°K for oxide components of leached residues from DWRG glass, kJ/mole.
- 7.5 Estimated free energies of formation at 373°K for oxide components of leached residues from DWRG glass, kJ/mole.
- 7.6 Estimated free energies of formation at 343°K and 373°K for oxide components of leached residues from PNL 76-68 glass, kJ/mole.
- 7.7 Estimated free energies of formation at 343°K for oxide components of leached residues from PGM glass, kJ/mole.
- 7.8 Estimated free energies of formation at 343°K for oxide components of leached residues from DWRG and CUBS glasses, kJ/mole.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

Chapter 7 emphasizes the generality of PROTOCOL while providing almost no information on deficiencies and limitations (except the broad outline of what PROTOCOL is intended to do). In particular, PROTOCOL models the waste form and not repository characteristics such as the hydrological flow, the chemical composition of inflowing groundwater, and the reactions of dissolved species after they leave the immediate vicinity of the waste form.

CONCLUSIONS OF AUTHOR

"A FORTRAN version of PROTOCOL contains 1) a kinetic capability to describe release from the glass, 2) an equilibrium capability based on the geochemical code MINEQL that models solution concentrations and precipitate formation, 3) a system-monitoring capability that directs the computations through a series of discrete time increments, and 4) a capability to estimate the standard Gibbs free energy function of poorly characterized solid phases."

"Conventional solubility considerations are also extended to non-stoichiometric alteration products of glasses.

COMMENTS OF REVIEWER

Chapter 7 is essentially promotional material for the software package PROTOCOL and not the documentation needed to justify the use of PROTOCOL for licensing purposes. Proper documentation of software has been extensively discussed in the literature. See A Survey of Techniques for Evaluating Emergency Planning Models and Data Bases, by R.E. Chapman, R.G. Hendrickson, S.F. Weber (NBSIR 84-2963, National Bureau of Standards, November, 1984). Proper documentation should answer the questions:

1. Considered as a computer device, can the model be understood and used by third parties?
2. What are the model's fundamental mathematical properties?
3. What is the model's logical (e.g., physical, statistical, engineering) structure? What is the domain of model application?
4. What is the nature of the data needed to implement, to prepare output reports, and to test the model?
5. Are the individual specifications and assumptions supported by data and theory?

6. What can be said about the reliability or uncertainty of the outputs?
7. How is the model used? For what purposes is it suited?

Chapter 7 address these questions, but not completely or coherently. By creating software that is very general, Lawrence Livermore National Laboratory may have created something that is indescribable, and thus useless for licensing purposes.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

- 2.3 when, how, and at what rate, will radionuclides be released from the waste form
- 2.3.2 what is the solubility of the waste form under potential repository conditions
- 2.3.2.1 what are the possible dissolution mechanisms of the waste form under the range of potential repository conditions?

(b) New Licensing Issues

(c) General Comments on Licensing

By creating software that is very general, Lawrence Livermore National Laboratory may have created something that is indescribable, and thus useless for licensing purposes.

Appendix D. Outlines of Interpretive Papers on Selected
Topics

Outline of the Interpretive Paper
Mechanisms of Environmental Induced Fracture and their
Relevance to HLW Containers in the Tuff Environment

I. Introduction

A. Purpose

B. Scope

C. What is Environmental Induced Fracture (EIF)

1. SCC
2. HE
3. LME
4. CF

D. What causes EIF

1. Environmental Factors
2. Stress Factors
 - what kinds of stress
 - how much stress
 - sources of stress in HLW containers

E. Quantifications

Since the mechanism of SCC is not known and since we don't even know if there is only one common mechanism or a host of different mechanisms, we have to discuss and evaluate what is known based on the types of experiments that have been conducted. As a result, we must discuss the techniques used to evaluate and quantify environmental induced fractures.

II. Environments Known to Cause SCC of Candidate Stainless Steels

A. Halide Containing Environments

B. Other types of Environments

C. Tuff Environment

- Review environmental species available in Tuff
- J13 Concentration
- Concentration Solns.
- Temperature Effects

III. Mechanism(s) of EIF

The mechanisms which have been proposed to explain EIF will be reviewed and evaluated with respect to their possibility of occurring in the Tuff environment. Only those mechanisms which are still considered to be viable possibilities by the EIF research community will be discussed.

IV. Avoiding SCC

A review of the techniques that can be used to avoid SCC will be presented.

A. Stress Control

B. Control of Environment

C. Modeling

1. Empirical modeling
2. Mechanistic modeling

V. Summary

VI. Conclusions

VII. References

Outline of the Interpretive Paper
Mechanisms of Localized Aqueous Corrosion of Copper and its
Alloys

I. Introduction

Copper-base metals have been proposed as alternative materials for the high-level waste containers at Yucca Mountain. Although it is reasonable to assume that these materials will perform satisfactorily, there are major uncertainties as to the environment that they will have to withstand, as well as to their behavior in certain circumstances. In particular, the possibility that copper-base containers may fail because of some form of localized attack, mainly stress corrosion cracking (SCC), cannot be easily discounted.

An additional cause of concern is that, in discussing the mechanisms and conditions leading to this kind of failure, the DOE Site Characterization Plan seems to be significantly at variance with the prevailing opinions among experts in the field.

II. Purpose

It seem appropriate, therefore, to undertake a review of what is currently known about localized corrosion of copper and its alloys, with particular emphasis on stress corrosion cracking, in order to put the problems into sharper focus, taking into account the Yucca Mountain repository environment and its uncertainties.

III. Scope

The environmental conditions in the repository, because of the best generated by radioactive decay, are expected to lead to dry oxidation of the metal containers for very long items. However, aqueous corrosion is a significant possibility, particularly if the conditions deviate somewhat from those anticipated. The present paper will not concern itself with dry oxidation, but will consider aqueous corrosion, whether due to liquid water percolating through the rock or moisture condensing on the metal surface.

IV. Body of the report

The proposed interpretive paper will be a review of localized corrosion in copper and copper alloys. The topics to be covered are:

- A) Pitting
- B) Stress Corrosion Cracking
- C) Intergranular Attack
- D) Crevice Corrosion

It is suggested that topic B will be the first to be addressed. A tentative scheme of the organization of the paper is as follows:

- 1) A description of the environments in which SCC has been observed
- 2) A list of the mechanisms which have been advanced for its explanation
- 3) A discussion of their relevance for the repository condition

Although the work will concentrate on the three Cu-base materials which have been selected by DOE, namely pure copper, Aluminum bronze and Copper-Nickel alloys, other materials, such as brass, will be included in the paper, since a great deal of the mechanistic work published has been carried out on brass.

This review will allow an assessment of the likelihood of container failure by SCC at the repository on the basis of what is already known, and will contribute to determining which information and data must be obtained before Cu-base alloys can be accepted or rejected as container material for high level waste.

V. Summary

VI. Conclusions

VII. Reference

Outline of the Interpretive Paper
Mechanisms of Internal Corrosion of Spent Fuel Rods

I. Introduction

- A. Most failures of Zircaloy nuclear fuel cladding until now have been internal resulted from mechanical, chemical and nuclear reactions.
- B. Considerations of spent fuel cladding for radionuclide containment may be included in determinations to assess whether the engineered barrier will meet release requirements.

II. Purpose

This paper will provide a review of information on mechanisms of previous failures, and it is intended to be useful for assessing corrosion and making long term durability predictions of Zircaloy cladding in a tuff repository.

III. Scope

This paper includes information on radionuclide containment requirements, previous cladding failures, causes of the failures, corrective measures taken by the nuclear industry and discussions of potential modes of internal failures that should be considered for long term repository storage.

IV. Body of the report

- A. Materials
 - 1. Metallurgical aspects of Zircaloy-2 and Zircaloy-4
 - 2. Stainless steel nuclear fuel cladding
- B. Environments
 - 1. Environments of previous failures
 - 2. Anticipated repository environments
- C. Failure modes and mechanisms
 - 1. Cladding collapse
 - 2. Pellet cladding interactions
 - 3. Hydride formation
 - 4. Fretting corrosion

- D. Effects on corrosion
 - 1. Temperature
 - 2. Ions
 - 3. Hydrogen
 - 4. Stress
 - 5. Oxidation, passivation

V. Summary

VI. Conclusions

VII. References