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Evaluation and Compilation of DOE Waste Package Test Data

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ABSTRACT

This report summarizes results of the National Bureau of Standards (NBS) evaluations of Department of Energy (DOE) activities on waste packages designed for containment of radioactive high-level nuclear waste (HLW). The waste package is a proposed engineered barrier that is part of a permanent repository for HLW. Metal alloys are the principal barriers within the engineered system. Since enactment of the Budget Reconciliation Act for Fiscal Year 1988, the Yucca Mountain, NV, site (in which tuff is the geologic medium) is the only site that will be characterized for use as a high-level nuclear waste repository. During the reporting period of August 1987 to January 1988, five reviews were completed for tuff, and these were grouped into four categories: (1) ferrous alloys, (2) copper, (3) groundwater chemistry, and (4) glass. Two issues are identified for the Yucca Mountain site: (1) the approach used to calculate corrosion rates for ferrous alloys, and (2) crevice corrosion was observed in a copper-nickel alloy. In addition, it is noted that plutonium can form pseudo-colloids that may facilitate transport. NBS work related to the vitrification of HLW borosilicate glass at the West Valley Demonstration Project (WVDP) and the Defense Waste Processing Facility (DWPF) and activities of the DOE Materials Characterization Center (MCC) for the 6-month reporting period are also included. Appended to this report are NBS reviews of selected DOE technical reports. Included here are selected other reviews which, although they were conducted under the basalt and salt programs, are considered to be relevant to the present work on the tuff repository program. For these former candidate sites, technical discussions are given for the corrosion of metals proposed for the canister, particularly carbon steels, stainless steels, and copper.

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EXECUTIVE SUMMARY

This is the fourth biannual progress report on the National Bureau of Standards (NBS) assessments of the Department of Energy (DOE) activities related to the waste package for disposal of radioactive high-level waste (HLW). It contains NBS reviews conducted over the period August 1, 1987, to January 31, 1988, on DOE reports related to activities of the Nevada Nuclear Waste Storage Investigation (NNWSI). Status reports given here highlight the NBS assessments of DOE activities of Yucca Mountain, NV. Reports from the Salt Repository Project (SRP) and the Basalt Waste Isolation Project (BWIP) which, in the opinion of NBS reviewers, are relevant reference materials for the Yucca Mountain Site are included in this progress report. In addition, a summary is given for the activities of the DOE-sponsored Materials Characterization Center (MCC).

The Budget Reconciliation Act of 1988 (Public Law 100-203) directed the DOE to terminate site-specific activities on both the Salt Repository Project (SRP) and the Basalt Waste Isolation Project (BWIP). Thus, only the Yucca Mountain, NV, site will be characterized as the potential high-level waste repository. Future NBS work will concentrate on research related to the Yucca Mountain repository site in the tuff geologic media.

In this report, five completed reviews dealing with the engineered barrier for the tuff site are included. In these, two issues were identified. The first is related to measurement techniques, and it deals with the approach used to calculate corrosion rates in ferrous alloys. The second is that crevice corrosion was observed in a nickel-copper alloy. Both of these issues are discussed here and both will be followed by the NBS. In addition, a conclusion is given on groundwater: plutonium can form pseudo-colloids and this may facilitate transport to the environment. In the area of glass-related studies, two topics that are briefly discussed are the drip (dynamic) test and the static leach test. Both tests are used to determine rates of radionuclide dissolution.

NBS activities related to evaluation of DOE programs at the West Valley Demonstration Project (WVDP) and the Defense Waste Processing Facility (DWPF) in the area of vitrification of HLW continue. This biannual report includes reviews on eight published reports and Chapters 1 and 7 of PNL-5157, "Final Report of the Defense High Level Waste Leaching Mechanisms Program." Reviews of many other reports have been initiated and will be included in later

biannual reports. The principal technical questions cited by NBS in relation to the DOE's HLW vitrification efforts are as follow: (1) will the leaching characteristics of proposed glass compositions be sufficiently favorable as to meet NRC criteria for radionuclide release from the glasses in the repository environment, (2) will the facilities and methods proposed for use at the DWPF and WVDP provide glasses of the specified compositions, and (3) will glass compositions and the homogeneity of batches be adequately verified during actual production?

Status of laboratory testing at the NBS is included in the Introduction of this biannual report. The objective of these laboratory tests is to confirm the accuracy of DOE data and the validity of the conclusions deduced from it. One of the tasks under the study "Corrosion Behavior of Zircaloy Nuclear Fuel Cladding" was a brief review of corrosion of Zircaloy. This review has been completed and will be released for comments to the NRC within the next several months. Publication of the results of the study "Pitting Corrosion of Steel Used for Nuclear Waste Storage" will be forthcoming.

During the 6-month period covered in this biannual report, database activities focused on preliminary tasks associated with converting the NBS/NRC Database for Reviews and Evaluations on High-Level Waste to a new database management system (DBMS) using the software Advanced Revelation®. The conversion is expected to be completed within the next 6-month period. Advanced Revelation® has improved support features for the user, such as menus and popup screens both of which permit multiple choices in the retrieval of data.

1.0 INTRODUCTION

This is the fourth biannual progress report on the National Bureau of Standards (NBS) assessments of the Department of Energy (DOE) activities related to the waste package for disposal of radioactive high-level waste (HLW). This report covers NBS work during the period from August 1987 to January 1988. As in the three prior biannual reports in this series, this volume discusses NBS reviews of the three proposed repository sites, the DOE program for vitrification of HLW, and the activities of the Materials Characterization Center.

When the Budget Reconciliation Act for Fiscal Year 1988 (Public Law 100-203) was approved, major changes were made to the Nuclear Waste Policy Act of 1982 (NWPA), and the Federal nuclear waste disposal program took on new directions. The DOE was directed to characterize only the Yucca Mountain, NV, as the proposed site for the first repository. Site-specific activities for the Hanford, WA, and Deaf Smith County, TX, sites were terminated. The NWPA Amendments state that if the Yucca Mountain site proves unsuitable as a repository, DOE is required to terminate site-specific activities and report to Congress.

NBS evaluations of NNWSI work are included in Section 2.0 of this report. In addition to considering ferrous alloys for use as container materials, copper and copper alloys are also being evaluated for the tuff repository site. Results of a study by W. H. Yunker and R. S. Glass on pertinent radiation effects on copper-base materials are discussed in Section 2.0.

Other reviews considered pertinent to studies of a tuff repository are given. These are reviews of works conducted under the Basalt Waste Isolation Project (BWIP) and the Salt Repository Project (SRP). They are presented as Sections 2 to 4 respectively. Relevance of the work cited to the Nevada Nuclear Waste Storage Investigations (NNWSI), where apparent, is noted.

The DOE is actively engaged in programs for the vitrification of high-level radioactive waste in borosilicate glass. Both the West Valley Demonstration Project (WVDP) at West Valley, NY, and the Defense Waste Processing Facility (DWPF) located at the Savannah River Plant in Savannah, GA, are expected to vitrify HLW in the near future. NBS activities in this area continue with eight published reports and two chapters of PNL-5157 being reviewed during this reporting period. Particularly in Section 5.0 (the DOE glass vitrification program) the results of the testing for BWIP and SRP supplement the body of knowledge on radionuclide leaching from glass and are thus considered to be relevant to the work for NNWSI.

Activities of the DOE-sponsored Materials Characterization Center (MCC) and the status of selected MCC test methods are discussed in Section 6.0. The MCC monthly reports over the past one and one-half years show considerable progress on test development work for glass leaching and materials durability in SRP and BWIP; however, the MCC has done very little work on the development of test methods for the tuff repository site.

NBS reviews and evaluations conducted over the period August 1, 1987, to January 31, 1988, are included as Appendix A; contributing reviewers for these reviews are acknowledged as a group on the cover page of this report.

Reviews are created using guidelines that are modified periodically. The guidelines describe for reviewers the types of information to be contained in each section of a review. The current version of the guidelines for reviewers is included in Appendix A (pp. A-6 to A-10).

Studies involving laboratory testing at the NBS are continuing in four areas. As the results of these studies will be reported separately at appropriate stages of the work, no reports on these studies are included in this report. The objective of these laboratory tests is to confirm the accuracy of DOE data and the validity of the conclusions deduced from it. Topics of these four studies are as 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, (3) Pitting Corrosion of Steel Used for Nuclear Waste Storage, and (4) Corrosion Behavior of Zircaloy Nuclear Fuel Cladding. One of the tasks under study 4 was a review of corrosion of Zircaloy. This review has been conducted and it will be released to the NRC for comments within the next several months. Publication of the results of study 3 is expected within the next 6-months. Results from the other laboratory testing will be also published upon completion of selected parts of these works.

During the 6-month period covered in this biannual report, database activities focused on converting the NBS/NRC Database for Reviews and Evaluations on High-Level Waste to a new database management system (DBMS), Advanced Revelation®. This DBMS has menu capabilities regarded to be superior to those developed at NBS for use with Revelation®. Conversion of the NBS/NRC files from the present DBMS, Revelation®, into Advanced Revelation® is expected to be completed over the next reporting period and it will create a more powerful and "user friendly" DBMS, and permit faster retrieval database. Advanced Revelation® has improved support features for the user, such as menus and popup screens both of which permit multiple choices in the retrieval of data. The earlier version, Revelation®, had been modified by the NBS to do many of these same things, but the NBS enhancements were not as complex as those permitted in Advanced Revelation®.

In addition, Advanced Revelation® informs the user about either what it is doing now or what the user should do next. In addition to the DBMS conversion, during this period the keyword checklist and keyword checklist tree were modified to incorporate a new key field which contains a separate set of keywords for non-metallic waste forms. Inclusion of the non-metallic waste form in the keyword checklist complements the NBS evaluation of DOE work in the vitrification of HLW at the DWPF and WVDP. (Appendix B of this report includes the revised keyword checklist tree and the revised keyword checklist.)

2.0 NNWSI -- NEVADA NUCLEAR WASTE STORAGE INVESTIGATIONS

Yucca Mountain is the proposed site of the nuclear waste repository, and is located approximately 100 miles northwest of Las Vegas, Nevada. The repository, as planned, will be located in an unsaturated, compacted volcanic ash commonly referred to as tuff. The level of the repository is 100 m above the water line, hence its unsaturated state, and approximately 400 m below the ground surface. Extensive research is being conducted by private and government laboratories in an effort to understand the problems involved in long-term disposal of nuclear waste at this site. Waste-Package related publications that result from these efforts are reviewed and evaluated by the National Bureau of Standards.

In this report, five completed reviews dealing with the engineered barrier for the tuff site are included. In these, two issues were identified. The first is related to measurement techniques, and it deals with the approach used to calculate corrosion rates in ferrous alloys. The second is that crevice corrosion was observed in a nickel-copper alloy. Both of these issues are discussed here and both will be followed by the NBS. In addition, a conclusion is given on groundwater: plutonium can form pseudo-colloids and this may facilitate transport to the environment. In the area of glass-related studies, two topics that are briefly discussed are the drip (dynamic) test and the static leach test. Both tests are used to determine rates of radionuclide dissolution.

2.1 Ferrous Alloys

Because of the low moisture content and limited soluble salts, the tuff environment may be presumed to be less corrosive than would an environment of higher moisture and salt contents. Nevertheless, when the long times of performance needed for a repository canister are considered, this notion may prove false. The tuff environment is expected to be oxidizing and this may accelerate the corrosion process for many metals and alloys, especially over the very long times at the elevated temperatures that are expected in the tuff repository. In addition, it is noted that in the life of the repository when temperatures are decreasing, moisture entering the zone of the repository will redissolve various salts that had been deposited in the tuff rock during the earlier high-temperature period (perhaps the first 50 y). This will have the following effects: (1) increase the boiling point of the incoming water, (2) bring liquid water into contact with the container sooner than one would estimate without considering the elevation of the boiling point, and (3) enhance the corrosivity of the environment during this early (<300 y) period. Hence, the environment is in many ways one that could substantially promote corrosion, and various types of local attack, which could greatly shorten the life of a container.

McCright et al., describe a preliminary study of the corrosion of stainless steel alloy canister materials. These materials were subjected to a simulated tuff environment over continuous exposure periods from 500 h to 2 months. Also described are results of similar studies on carbon steels for use as borehole liners and overpacks. Using slow-strain-rate techniques, the relative susceptibilities of 304L to stress corrosion in the annealed and sensitized conditions are compared. [Ed. The 304L specimens were solution annealed 1050°C - 15 min water quench and then sensitized at 600°C for 10 h and air cooled to simulated glass waste pouring]. All failures were observed to be ductile, indicating no apparent susceptibility to stress-corrosion cracking. Four-point bent-beam tests of these and other stainless steels are underway. Electrochemical polarization techniques were applied for measuring the corrosion of coupons in simulated irradiated and non-irradiated repository conditions. These tests indicate that the corrosion rates in all cases are less than 50 μm/y, and reveal that the 9Cr-1Mo alloy underwent more attack during the 1000 h exposure than AISI 409, 416, 304L, 316L, and 317L, but, as expected, not as much attack as the carbon steels. In all cases, the 9Cr-1Mo alloy sustained greater attack under gamma radiation than under similar conditions without radiation. In 2 out of 12 cases, the 304L stainless steel sustained greater attack in the presence of gamma radiation than under similar conditions without radiation. Cyclic anodic polarization tests were also performed to evaluate the tendency of these materials to pitting. The test indicated that, under the test conditions, these materials showed no evidence of localized attack. Results are preliminary, and will be followed by further testing [McCright et al. 1984].

An NBS concern is that the calculated penetration rates of the ferrous alloys are unrealistically low because metal weight loss is attributed to uniform attack over the entire surface of the coupon; corrosion, however, may be localized. The result of this approach is that calculated penetration rates are unrealistically low.

2.2 Copper

In addition to considering ferrous alloys for use as container materials, copper and copper alloys are also being evaluated. The corrosion resistance of three materials, pure copper, 7 percent aluminum-copper, and 30 percent nickel-copper, tested in water and water-vapor phases at elevated temperatures, with and without radiation is evaluated in this study [Yunker et al. 1986]. After 14 months of exposure, the corrosion rates observed are low, less than 13 $\mu m/y$ (< 0.5 mils per year), and these preliminary observations indicate that the corrosion rate of the 7 percent aluminum-copper is less than that of the pure copper. The results on the 30 percent nickel-copper are erratic, and pitting and crevice corrosion were observed on this alloy between an alumina washer and a flat specimen. To a more limited extent, on the other two materials pitting and crevice corrosion were also observed.

2.3 Groundwater

Present knowledge about the corrosivity in tuff is based on the chemical composition of water samples taken from a well near the proposed Yucca Mountain repository site. This J-13 well water has a low concentration of soluble salts, and is considered relatively noncorrosive. However, in the presence of gamma radiation from the nuclear waste, water is expected to undergo chemical changes, some of which may result in increased corrosion attack on the canister materials and subsequent increased dissolution of the waste.

Ebert et al., describe a study in which small coupons of waste glass and Topopah spring tuff are placed in J-13 spring water in the presence and absence of radiation. The plots give data taken at each of 5 to 7 periods of exposure, each lasting from 14 to 280 days. After exposure, the tests were stopped, the water analyzed, and the coupon surfaces examined. The results show that nitric acid is formed in the radiation field, but buffering effects will limit the pH to a minimum of about 6.4. Most importantly, however, the data indicate that plutonium can form pseudo-colloids and this may facilitate transport to the environment [Ebert et al. 1986].

2.4 Glass Waste

Once the canister, the primary barrier, is breached, groundwater is free to contact the radioactive waste. Thus, the interactions between groundwater and the radionuclides contained in the canister and the effects of these interactions on radionuclide release to the environment are major concerns.

Bates and Gerding describe a test for measuring radionuclide release rates in which tuff groundwater is dripped onto a waste glass assembly for 13 and 26 weeks. Radionuclide release rate is determined from analysis of the water collected and analysis of the assembly surfaces. The authors indicate that the results of these tests show that this method of testing provides reproducible results and realistically simulates repository conditions [Bates et al. 1985].

Bibler performed a static leaching test which presumably follows the techniques described in MCC-1 "Static Leach Test for Waste Glass." The author uses Teflon® holders, as prescribed by MCC-1, in an earlier series of tests, and stainless steel holders in the more recent study. He notes that radiolysis of Teflon® increases the dissolution rate of glass, and by using stainless steel containers this adverse effect is avoided. The 1985 version of the MCC-1 static leach test addresses this issue and states that "The total integrated dose for each Teflon® leach container or any Teflon® supported structures may not exceed 10^4 rad during the lifetime of the containers." The author also concludes that surface finish of the specimen is a critical factor in obtaining reproducible data. This effect of surface finish is also taken into consideration in the lastest version of MCC-1. Radiolysis of water has little effect on leaching rates: radioactive and nonradioactive glasses leach at the same rate [Bibler 1986].

3.0 BWIP -- BASALT WASTE ISOLATION PROJECT

3.1 Reviews

Two major problems in assessing the corrosion resistance of candidate materials (the effect of γ-irradiation on corrosion and the rate of pit growth) were examined in two reports which were reviewed in the past 6 months and are considered potentially relevant to studies of a tuff repository. The first, by Nelson, studied some low-alloy Fe-base and Ti-base materials at temperatures as high as 250°C and exposed to intense γ-radiation of up to 2×10^6 rd/h. For the Fe-base alloys a 2- to 3-fold enhancement in the corrosion rate was observed. However, extrapolation to the much longer times actually required is very doubtful, as there are no data showing that the corrosion mechanisms are the same at higher and lower temperatures. Titanium Grade 2 and Grade 12 showed excellent corrosion resistance under irradiation, but hydrogen absorption was detected. The hydrogen presumably is generated by radiolysis, and although insufficient to cause embrittlement after only a 10-month exposure, hydrogen levels may approach embrittling levels over longer exposure times [Nelson et al. 1983].

The second report discussed experimental and modeling studies of pit propagation in carbon steel. The results show the importance of pit wall reactivity on pit propagation rates. The pit propagation rates obtained either in experiments or in modeling studies are affected by the pit wall behavior, i.e. whether or not pit walls are made to participate in the electrochemical reactions. A possible conclusion from these studies is that pit penetration rates, as measured in a number of laboratory experiments where the simulated pit walls could not corrode, may be unduly pessimistic. Another interesting conclusion is that environments promoting active corrosion do not support pit propagation even when a differential aeration or a pH cell is established. These studies are necessary for assessing the seriousness of pitting as a failure mode for waste containers, but are still far from providing the numerical values needed for modeling [Beavers et al. 1987].

3.2 Copper

In recent times there has been renewed interest in the use of Cu-base alloys as the material for waste containers, and this interest extends to present work on the tuff repository. As a consequence, a preliminary feasibility study was reported for a basalt repository [Duncan 1986a]. On the basis of very limited testing, the author concludes that copper is a viable candidate material. The NBS examination of the corrosion test results, however, shows large scatter in the data, indicating that uncontrolled but significant factors are at work. This may only be a consequence of poor test design, but optimism so far is unwarranted.

An elaborate method for the analysis of gases dissolved in groundwater has been developed, as reported by Halko 1986. One hopes to see publication of extensive experimental results. Both for site characterization and for calculating rates of radioactivity release, it is important to study the interaction between radionuclides and the environment. Salter et al. have measured the sorption behavior of a number of radioactive isotopes on Columbia River basalts under various conditions of temperature, pressure, and groundwater composition. The authors conclude that these rocks strongly retard Cs, Sr, Ra and Np migration, but this conclusion requires further calculations concerning the available sorption surface area and groundwater flow rate [Salter et al. 1981].

Several papers on stress corrosion cracking (SCC) and environmentally assisted cracking (EAC) were reviewed during this period. These will serve as references for reviews of similar studies expected for various candidate canister materials presently being considered by NNWSI. Each gives experimental procedures and results of preliminary tests conducted for basaltic environmental conditions. In one of these, the need for a more sensitive method for detection of cracking extension in fracture mechanics specimens becomes very evident; there is uncertainty on whether or not crack extensions actually occurred. After using both optical and compliance techniques, the researchers remained in doubt on the question of crack extension [James 1985]. The second of these papers is a progress report that gives results of fatigue tests of several materials (A36, A27 and A387 Grade 9 steels) tested in air at 150 and 250°C [James et al. 1984]. The last paper in this group gives procedures for and results of slow-strain-rate and fracture-mechanics tests of three steels (1020, A27 Gr 60, A387 Grade 9), OFHC Copper (UNS C10200) and 90-10 cupronickel alloy (UNS C70600), [Duncan et al. 1986b].

3.3 Conclusions

Although at present a basalt repository is no longer the primary choice, work carried out so far does not indicate that such a repository would be unsuitable. Which candidate material for waste container construction is best and whether it can satisfy the containment requirements, is still an open question. For instance, hydrogen embrittlement cannot be excluded as a possible cause of early failure for Ti alloys, while the effect of radiation on the corrosion reactions of Cu-base alloys is not known with sufficient certainty to predict their behavior under repository conditions.

4.0 SRP -- SALT REPOSITORY PROJECT

It is noted that if NNWSI decides to consider carbon steels, some of the data collected under the SRP project will be of value because the first water to reach the container will contain concentrated salts. If carbon steels are not considered by the NNWSI, then the experimental methods utilized may still be of value for testing the selected alloy in tuff environments.

The site selected for the salt repository project was in Deaf Smith County which is in the southern high plains of the Texas panhandle 35 miles southwest of Amarillo. The proposed repository site was 2,400 to 2,500 feet below the surface and approximately 1,000 feet below the aquifer which supplies much of this region with irrigation water. The rock salt bed at this site is approximately 160 feet thick and is the result of the drying of a salt lake during the Permian Age. As a result, the salt bed would have contained water inclusions and many impurities which would have made prediction of long-term behavior difficult. Several problem areas connected with the development of this site have been identified:

- The repository environment was inadequately characterized.
- The validity of the limited brine assumption needed to be thoroughly evaluated.
- Alloy selection required resolution of the limited versus unlimited brine approaches to repository analysis.
- Testing container alloys in representative environments required better characterization of the environment.

- Very few tests of waste form in brines were undertaken because of the emphasis on the limited brine assumption.
- Little consideration was given container closure methods and the impact of this on the corrosion behavior of the container.
- Quality assurance was inadequate and too reliant on peer review rather than on the quantitative results of experiments.
- Long-term exposure tests were needed for representative environments used for tests of samples of the container alloys in each possible metallurgical conditions (weld zones, etc.) were needed.

Based on these factors, NBS reviewers concluded [Interrante et al. 1987a] that serious obstacles remained which would make licensing the Deaf Smith site difficult.

4.1 Reviews

During the period covered by this report, review of one report was completed prior to termination of the reviewing process for this site. [see Appendix A, p. 72]

In PNL-5426, [Westerman et al. 1986] present a detailed review of broad-based corrosion studies used to assess the suitability of ferrous materials for use as waste-package overpack. The program reviewed addresses general corrosion in simulated inclusion and intrusion brines, irradiation effects and environmental cracking based on slow strain rate, and corrosion fatigue tests. The report acknowledges the potential importance of bacterial corrosion and hydrogen embrittlement in an overall degradation model, but does not reference related data.

5.0 VITRIFICATION OF HIGH-LEVEL WASTE

NBS activities in high-level waste (HLW) vitrification provide NRC with technical information on the acceptability of vitrified waste for disposal in a repository. The NBS objective is accomplished by technical assessments of work performed by DOE, DOE contractors, and other laboratories.

5.1 Technical Issues

The principal technical questions in relation to the DOE's HLW vitrification efforts are as follow: (1) will the leaching characteristics of proposed glass compositions meet NRC criteria for radionuclide release from the glasses in the repository environment, (2) will the facilities and methods proposed for use at the Defense Waste Processing Facility and the West Valley Demonstration Project provide glasses of the specified compositions, and (3) will glass compositions and the homogeneity of batches be adequately verified during actual production?

The major portion of NBS activities during the current reporting period continued to deal with the first of these questions, i.e. leaching behavior. Two reports reviewed in this period relate to the other questions [Barnes 1986 and DOE 1986]. NBS reviews of leaching test results indicate a general need for more testing and for tests of longer duration. The first six reviews mentioned below deal with projects that have general applicability to leaching in any environment. Test results for the Basalt Waste Isolation Project were nearly complete at the time of the deletion of two potential repository sites and, were, therefore, completed rather than discarded.

One of the reports reviewed indicated that for predictions of long-term behavior, a pulsed-flow test that used powdered glass for test specimens was superior to either static tests or frequent-exchange tests, both of which used glass blocks [Barkatt et al. 1986]. The pulsed flow technique measures leach rates under conditions in which the leachate composition is near saturation. Thus, this test may be more relevant to conditions in the tuff repository. Although the tests reviewed during this reporting period did not deal directly with leaching in tuff groundwater, background information concerning glass leaching is provided.

5.2 Reviews

NBS reviews of eight published papers and of Chapters 1 and 7 of PNL-5157 have been completed during this past six months. Five papers and Chapters 1 and 7 of PNL-5157 deal with various aspects of glass leaching. Of the other three papers, one summarizes a plan for the Savannah River Plant's interim waste management programs, another summarizes experimental results of procedures and equipment tests of the West Valley Vitrification Demonstration Project, and the third deals with the effect of radiation on the glass surfaces.

5.3 Reviews of General Glass-Leaching Studies

A review of Chapter 1 has been completed [Barkatt et al. 1984, see Appendix A, p. 81]. The chapter provides experimental data and a literature review of glass corrosion studies. These help to describe the basic mechanisms of glass leaching and corrosion. Although the chapter does not succeed in its main goal of predicting long-term leach rates by quantitatively describing the leaching of the glass matrix in terms of specific variables, it does provide general indications of trends in leaching behavior. The chapter provides largely qualitative information about the following parameters in glass leaching: glass composition, leachant flow rate, temperature, leachant composition, protective films, and repository conditions. The methodology and the validity of the data are also discussed. A major problem is the lack of a definition of "abnormal" repository conditions and the lack of study of such abnormal conditions on glass leaching.

A review of Chapter 7 has been completed [Mendel 1984, see Appendix A, p. 93]. This chapter deals with a computer program, PROTOCOL, which simulates the dissolution reactions of solids with aqueous solutions. The reviewers state that the chapter provides neither a complete documentation of the software, nor references that could direct the reader elsewhere for full documentation. These comments refer to the description of PROTOCOL and not the general utility of the program which has not been fully explained in Chapter 7. However, PROTOCOL appears to do the same type of modeling calculations envisioned for EQ3/6, which appears (in the recent literature) to be the modeling program of choice. Thus, PROTOCOL may be a duplication of effort in the modeling task.

Three papers from the Catholic University Vitreous State Laboratory were reviewed. The purpose of the work in Barkatt et al. 1986 was to characterize the leaching durability of the currently proposed West Valley Reference Glass (WVRG) in comparison with the Defense Waste Reference Glass (DWRG) as well as to investigate the behavior of two other glasses having acceptable melting and viscosity ranges for processing. The report presents leach data for four glasses using three types of leach tests. The data do substantiate that, under the test conditions used, West Valley Reference Glass (WVRG) and Defense Waste Reference Glass (DWRG) are similar in behavior and are both considerably more durable than glasses A and B, which are designed to be processible. The modified IAEA/ISO test indicated that the dissolution was nearly congruent except for highly insoluble components such as Fe and Mn. The MCC-1 tests showed no significant differences between the WVRG-I, WVRG-II, and Defense Waste Reference Glass (DWRG) during the corrosion process, which was nearly congruent. Pulse-flow tests, carried out with powdered glass samples and high S/V ratios, indicated saturation effects for all four glasses. These effects resulted in suppression of leach rates of all glass components. The normalized elemental release rate of the WVRG glass is about 20 percent greater than the DWRG glass.

At a workshop on leaching mechanisms, Barkatt et al. presented data showing that the solubilities of diverse glasses could be correlated with the pH and the product of Al and Si concentration in the glass at a constant temperature of 70°C. This was not a straight-line correlation. The solubilities increased more rapidly with pH between 9.5 and 12 (slope of 1) than between 7 and 9.5 (slope of 0). They hypothesized that the solubilities of aluminum and silicon are controlled by the presence of an equimolar alumina silica compound which is re-adsorbed on the glass surface thereby controlling the solubility of the glass. At a slow flow rate, such as in geologic repositories, the solubility is controlled by the temperature and the pH of the leachate according to this correlation. If the limits of these parameters are known, predictions of long-term leach rates can be made. However, minor glass constituents are expected to leach much more slowly in the slow-flow conditions of the repository. This decreased rate of leaching is attributed to the aluminosilicate-saturated region, which blocks the minor constituents from exposure to the leachate. The slower release of minor constituents may be due to reincorporation of the altered aluminosilicate into the composition of the glass. The authors of the report point to the need for additional data [Barkatt 1982].

5.4 Reviews of Glass-Processing Reports

An excellent summary of the plan for the Savannah River interim waste management programs was also reviewed. The report describes the project administration, source of funds, status of each part of the program, the waste form generation including process flow chart and the waste radiological and chemical characteristics, the waste management facilities, waste inventories, schedules, major milestones, and the environmental monitoring program [DOE 1986].

A review was conducted on a report that summarizes the experimental results of tests of the operating procedures and equipment of the West Valley Vitrification Demonstration Project. Full-scale tests of the process equipment have been conducted with nonradioactive materials. General descriptions of the processes and the equipment were given along with the results of initial experiments from preliminary tests. Seventeen process runs have been conducted. In these runs, simulated waste glass slurry (a total of 41,500 l) was fed to the melter and the product glass (28,400 kg) was collected. Several problems which must be solved were identified as a result of these runs. Cracks, which may occur in the glass blocks, must be measured because the leach rate may depend on surface area. The authors propose to solve problems of feed segregation in the concentrator by addition of certain elements to the slurry. It is unclear that these problems will be solved without significantly changing the composition of the glass. The NBS reviewer recommended occasional sampling of the glass [Barnes 1986].

5.5 Reviews of Glass-Leaching Studies in BWIP and Salt Environments

As part of the Basalt Waste Isolation Project, hydrothermal experiments have been designed to investigate the radionuclide release characteristics as a function of time, temperature, and waste package components. A series of tests were conducted at 150°C for periods of up to 6 months, using two different glasses and two different groundwaters. The SRL-165 glass was found to be more durable than SRL-131 (a glass with higher alkali and lower silica contents) in the presence of basalt groundwater. The authors concluded that tests of longer duration are necessary to determine if steady-state conditions were achieved. The behavior of Pu was not fully explained; more data are required to understand the behavior of this very important radionuclide. Aspects of this study were not performed in accordance with approved procedures; accordingly, the NBS reviewers concluded that these data cannot be used for licensing [Lane et al. 1985].

Leaching studies of PNL 76-68 prototype borosilicate waste glass conducted in Mg-rich brine under hydrothermal conditions showed that the concentration of Si in the brine solution was lower (by an order of magnitude) when compared with that of Si in deionized water under similar conditions. These high-pressure tests conducted by the Pennsylvania State University used non-standard methods. In these experiments, it was also observed that the extraction of Sr and Ba was about two orders of magnitude higher. Cs and Rb were about a factor of 10 more concentrated in the brine when compared with that in deionized water. Because Sr and Cs are the main radionuclides in nuclear waste, it is very important to develop a theory to explain these results. The Na-K exchange front was the most prominent feature of the chemical concentration profiles. Na diffuses out of the glass and K diffuses in because the activity of the Na is higher in the glass. The alkali ions are more mobile than other ions, and the exchange front penetrates most deeply into the glass [Komarneni et al. 1982]. NBS reviewers concluded that because aspects of this study were not performed in accordance with approved procedures, these data are not useful for licensing.

5.6 Radiation-Damage Study

The effect of radiation on the surfaces of silica and borosilicate glasses was studied in Italy and the report, published in "Nuclear Instruments and Methods in Physics Research," was reviewed. Radiation damage was studied by etching tests, by correlating the bleaching of color centers with thermal annealing, by estimating volume expansion via counting and measuring bubbles formed, and by calculating penetration depth [Manara et al. 1984]. The authors did not provide full information on the dose dependence and saturation behavior. In addition, there is no indication of the effect of the radiation damage on the leach rate. Evidence in the literature of radiation damage influencing leach rate is contradictory. Further study is required to determine leach rates in radiation-damaged glass.

6.0 MCC -- MATERIALS CHARACTERIZATION CENTER

The Materials Characterization Center (MCC) was established by the Department of Energy (DOE) in 1980 to ensure that qualified materials data are available on nuclear waste materials. This purpose is being met by: (1) developing standard test methods and having them approved, (2) testing nuclear waste materials using approved test methods, and (3) publishing test procedures and data in the Nuclear Waste Materials Handbook. Test methods and data packages are submitted to the Materials Review Board (MRB) for approval. The MCC and the MRB, organizationally, are under the Materials Integration Office (MIO), which is based in Chicago, Illinois. The MRB is made up of individual scientists from government and academia. The MCC is located in Richland, Washington, and is operated for the DOE by the Pacific Northwest Laboratories (PNL) of the Battelle Memorial Research Institute. The usual staff level of the MCC is ten people.

The MCC is supported at a level of approximately 60 percent from DOE, and the remainder of MCC's funding comes from other DOE offices dealing with nuclear waste materials and nuclear waste storage. The MCC prepares monthly reports in addition to project reports and other various reports submitted to its supporting offices.

The MCC monthly reports are divided into the following categories.

A. Program Administration
B. Quality Assurance (QA)
C. Support to the Office of Geologic Repositories (RW-23)(OGR)
D. Support to the Salt Repository Project (SRP)
E. Support to the Basalt Waste Isolation Project (BWIP)
F. Support to the Defense HLW Technology Program (DP-12)
G. Support to the Transportation Technology Center (TTC)
H. Support to the West Valley Demonstration Project (NE-20)(WVDP)

Activities conducted under Salt Repository Project (D) and the Basalt Waste Isolation Project (E) have been discontinued due to the selection of the Nevada Nuclear Waste Isolation Site in December 1987 as the only repository site to be characterized. Additional funding will be received from the Savannah River Defense High-Level Waste Technology Program, and work in this area will be increased.

This report is a brief summary of MCC activities from July 1, 1987, through December 30, 1987. The reader is referred to the MCC's monthly reports for further details.

6.1 Program Administration

The organization of the MCC has remained essentially the same as that reported in Figure 1, p. 18 [Interrante, et al. 1987b].

The MCC manager met with officials from Nevada Nuclear Waste Storage Investigations (NNWSI) to discuss future MCC support to the NNWSI. Program discussions were held with the Savannah River Laboratory to discuss work for FY 1988. Program plans and submissions for management approval of costs not covered by formal authorization were made.

MCC presented three invited papers at the Oak Ridge Waste Management Technology Center Workshop on Leaching Tests. The papers were entitled "Experience with MCC Leach Tests: Interlaboratory Comparison Tests and Reference Leach Test Data," "History of Leaching Tests: Radioactive Wastes," and "Standardized Chemical Durability Tests Developed by the MCC." Another invited paper was presented at the American Chemistry Society Meeting in New Orleans, Louisiana.

A representative from the Commission of European Communities (CEC) visited the MCC to discuss the ongoing round robin [Interrante et al. 1987c, p. 18] and its relationship to the BWIP/MCC-14.4 compliance test. Another visitor from the CEC came to discuss spent-fuel characterization. The MCC Waste Form and Analytical Standards task leader participated, by invitation, in the US/FRG Workshop on "Glass Development and Product Quality" in October 1987, and presented two papers entitled "Evaluation of Analytical Data as Determined by Round Robin Methods" and "Fabrication and Characterization of Materials Characterization Center Reference Glasses."

A briefing was held on the DWPF canister impact testing. Representatives from Sandia National Laboratories, GA Technologies, and DOE-Albuquerque attended.

6.2 Quality Assurance

The semiannual MCC evaluation of Nonconformance Reports, Deficiency Reports, Surveillance Reports, audit findings and Corrective Action Requests was completed in July 1987. A letter report entitled "MCC Evaluation of Conditions Adverse to Quality" was prepared and sent to the PNL. Training activities continued on test planning, project scope, software control procedures, etc. Surveillance reports were completed in the 6 months since July 1987 in areas including software control, glass data traceability, and analytical chemistry supporting the spent fuel task. An external audit of the MCC by the WVDP was completed in October 1987. While there were findings and seven observations in the areas of oven temperature profiles and calibration records, procedural adequacy, material control, QA plan revision and software control, the QA was considered effective and adequate.

The MCC records generated for SRP and BWIP were collected and sent to the MCC Record Center and were sent to the SRP and BWIP projects. Records indexes were revised and updated.

Records for Approved Testing Material (ATM), ATM-5 and ATM-6, will remain at PNL until an adequate lifetime storage facility is available. Specimens of ATM-10 glass were identified for archiving.

The OGR Readiness Review Supplemental Quality Assurance Requirements document was reviewed. Internal corrective actions resulting from internal audits were found to be adequate.

A deficiency report was issued due to a loss of power causing loss of temperature control in the brine stability experiment. The report was closed when data evaluation showed that temperature had little effect on the brine composition.

6.3 Support to the Office of Geologic Repositories (RW-23)

Test development work, American Society for Testing and Materials (ASTM) activities, spent-fuel analysis and operations, interactions with the Commission of European Communities (CEC) and some database work are included in this activity. The CEC round-robin test described uses a granite host rock.

As a result of the MCC Analytical Methods Workshop held in April 1987, the Ames Laboratory at Iowa State University will work with the MCC to study the merits of two main types of Inductively Coupled Plasma (ICP) instruments, atomic emission (AE) and mass spectroscopy (MS). The MCC will supply appropriate reference, calibration, and study materials, and the Ames Laboratory will provide funding for its own work. A round robin for analysis of powdered simulated nuclear waste glass was started for the participants of the MCC Analytical Methods Workshop. Five laboratories have submitted their data for this round robin, and data from two other laboratories are expected. The data are being collated, analyzed, and distributed. Initial review of the data shows that within a laboratory, there is a relative precision of 3 to 4 percent and this is typical of routine ICP methods.

Characterization of ATM-105 continued, and gamma scanning was completed for four boiling water reactor (BWR) rods. Gamma scanning was initiated for another lot of ATM fuel rods and will be completed in FY 1988. Fission gas sampling of one rod showed approximately 112 cm^3 of fission gas, and in another rod the sampling showed almost four times this amount. In later attempts to fission-gas-sample BWR fuel rods, the wall plug lens appeared to be radiation damaged. Another lens was ordered, and it will be installed. The system used for fission-gas-sampling will be recalibrated.

Calculations showed that the new Criticality Safety Specification (CSS) batch limits could be met for an ATM-103 and ATM-104 or for an ATM-103 and ATM-106, but could not be met to segment a third rod. A new storage container is being designed to solve this problem.

Two ATM-105 rods were sectioned for characterization. To date, ATMs-103, 104, 106 and two ATM-105s have been sectioned to produce 137 analytical samples and 31 fuel sections for storage and future testing. Photomicrographs were taken of ATM-105 as-polished specimens to examine fission product particles and inner and outer oxide layers on the cladding. Samples of ATMs-103, 104, 105, and 106 were examined with transmission electron microscopy (TEM), and the common five-metal epsilon-ruthenium phase was found with some barium zirconate particles within the ruthenium phase. The five-metal epsilon-ruthenium phase consists of the elements, Mo, Tc, Ru, Rd and Pd. This phase usually is found in the micron particle size range near the center of fuel which has been exposed to high temperatures. The use of TEM revealed this phase in the nanometer particle size range and showed that the phase was present in other areas and at the edge of the fuel. Details of this work will be given in the ATM-103 report. ATM-104 showed the presence of particles with up to 50 percent xenon. This was observed earlier in ATM-101 and may be common in LWR fuels.

MCC has generated over 100 different samples. The MCC sample inventory system will be computerized. A detailed inventory of all MCC ATMs was started. This inventory will provide a means of verifying control and availability of ATMs and of disposing of unneeded specimens used in preparing the ATMs.

Radiochemical analyses for ATMs-104, 106 and 105 were completed. Draft reports have been prepared on the characterization of ATMs-103, 104 and 106. Work is nearly complete on meeting software control procedures for license related work which apply to ORIGEN-2. Work will be planned to develop a method for analyzing the C-14 content of crud on the outer surface of fuel rods. NNWSI requested that samples of ATMs-101, 103, 105 and 106 be transferred to Argonne National Laboratory (ANL). Two sets of ATM-103 have been transferred to Oak Ridge National Laboratory (ORNL) for spark source mass spectrographic analysis.

MCC interacts with ASTM Committee C26 on Nuclear Waste Materials. The MCC-1 Static Leach Test was balloted at the ASTM subcommittee/committee level, and two negative votes were received. One negative vote related to clarification of the precision and bias section, the other related to the description of the oxygen fugacity control as a reference condition. Revisions will be made to reflect changes resulting from the negatives, and the document will be reballotted at the subcommittee/committee level.

MCC is participating in CEC round-robin testing. The test involves repository simulation with measurements taken every 28 days. The test uses granite host rock with smectite and sand packing materials, and a SON 68 glass waste form in a volvic water leachant under lifetime repository conditions. Testing is proceeding on the first year of these tests.

6.4 Support to the Salt Repository Project

This activity is being discontinued due to the selection of the NNWSI site. The SRP project dealt with a number of topics including test method development, workshops, etc., Many of these activities have been described in previous NBS reports [Interrante et al. 1987a, b, and c].

During this 6 month period, development of a pH sensing electrode and of pH and Eh reference electrodes continued. All capital items for this task have been received. The autoclave was installed and operated at 200°C both with deionized water and with 6 molal NaCl. Zirconia pH sensors gave a perfect pH response and were stable in 6 molal NaCl except for one which failed. Indications are that the system is suitably designed to complete the task, and a letter report on operational characteristics of the autoclave system was sent to the SRP. Measurements at 100°C and 150°C in 6 molal NaCl were made in the development of the pH electrodes. Measurements were also made at 200°C. Correction factors for using a 0.1 molal KCl reference electrode are 0.33, 0.39 and 0.42 for 100, 150 and 200°C, respectively. A letter report on the electrodes development task was sent to the SRP.

Liaison with the Lawrence Berkeley Laboratory (LBL) and external peer review continued, and a draft of the SRP-LBL-1 Solubility Test Method was prepared. The status of MCC work in support of SRP was presented at the SRP review in August 1987.

Laboratory tests to determine the compositional stability of PBB-3 brine continued. The last scheduled brine samples were taken in August and analytical data were entered into a computer to facilitate data reduction. A report entitled "An Experimental Evaluation of the Stability of a Simulated, Site-Specific Brine, PBB-3" was prepared and sent to the SRP. The report states that brine solutions were stable over a 131-day period within the uncertainty of the measurements. A precipitate formed in filtered brine stored at 20°C, but the composition of the brine did not change. Ten salt samples have been submitted for x-ray diffraction and scanning electron microscopic analysis.

6.5 Support to the Basalt Waste Isolation Project

Development of MCC/BWIP-14.4 Waste Form Compliance Test Method continued, and testing was begun using ATM-11, a Savannah River production glass and ATM-10, a simulated WVDP production glass. Testing continued but samples were not analyzed because funding was not secured. In October, all new work on the MCC/BWIP-14.4 project was halted due to funding uncertainties.

6.6 Support to the Defense High Level Waste Technology Project

This activity involves test method standardization, reference and testing materials, a database, waste form durability, canister materials performance, models, and thermal and processing properties. Planned test method standardization activities for this year were completed. Work on the comprehensive database is described in Section 6.9 of this report. No funding was provided for fabrication of the Hanford Waste Vitrification Project (HWVP) glass, ATM-18.

6.7 Support to the Transportation Technology Center

Pressurized flaw leak tests were performed on two Defense Waste Production Facility (DWPF) canisters. These tests were performed for the Transportation Technology center (TTC). All tests are complete and reports were submitted on schedule. Results of the tests showed that the canister shell was not breached by impact. Changes in canister dimensions resulting from the 9.1 m impact (accident canister) were five to seven times greater that changes after the 0.3 m impact (transportation canister). Indications were that glass fines were created by the 9.1 m impact, and fines in the 0.3 m were formed before impact.

One canister, referred to as the transportation canister, was impacted from a distance of one foot and had been transported. The other canister, referred to as the Accident canister, had been impacted from 30 feet.

The plenum of each canister was pressurized and amounts of glass fines exiting from flaws was determined. Pressure used with the transportation canister was 2 psig and the design flaws were 7/64-inch-diameter holes. For the two locations tested on this canister, 0.0029 and 0.0012 grams of glass fines exited. The accident canister was tested with 3 psig and design flaws were 3/8 inch in diameter. Exiting glass fines for four flaws tested in this canister were 0.0794, 0.3329, 0.2089, and 0.1068 grams. Initial plans were to use an aerodynamic particle size (APS) analyzer to determine particle size, but the APS detected no substantial difference in size of glass fines exiting and was able to measure sizes only up to 15 μm. The APS may have been damaged by the glass fines. It was decided that size distribution of the fines would be made with the scanning electron microscope and that HIAC analyses would be conducted of the material on the filters.

Glass fines from hole number six of the accident canister amounted to 332.9 mg with a maximum size of <149 μm. Glass fines exiting from hole number one of the normal canister were 2.9 mg in amount and had a maximum size of <20 μm. These are examples of maximum amounts and sizes. MCC provided tabulations for the different holes and the amounts in different size ranges for each hole. The analysis for canister A-10 impacted under accident conditions gave a total of 1699 kg material released from all holes and sizes of fines ranging from <10 μm to <4 mesh. These data are tabulated with a detailed breakdown according to size and amount of a given size. Canister A-27 impacted under normal conditions gave a total of 1667 kg released from all holes with sizes ranging from <10 μm to <4 Mesh.

A program status report was made at the November meeting of the DHLWTP in Salt Lake City Utah.

6.8 Support to the Defense Waste Processing Facility (Savannah River Laboratory)

A borosilicate glass standard, National Bureau of Standards (NBS) Standard Reference Material (SRM) 623 was received. This glass will be used for round robin testing. It is being crushed and sieved according to instructions of the Product Consistency Test (PCT). The SRL PCT method was reviewed and commented on by PNL staff.

6.9 Support to the West Valley Demonstration Project

This activity deals with reference glass durability testing, characterization and documentation of some ATMs, fabrication of some ATMs, and a database.

All MCC-3 leach testing has been completed and is undergoing internal review. MCC-1 testing of all glasses has been received except that from the Catholic University of America (CUA).

Pulsed-flow testing continues for the ATM-10 glass and the CUA glass. Pulsed-flow testing was completed for the West Valley Test Standard (CTS) glass. This completion was based on the stabilization of the boron release indicating that the glass dissolution has stabilized. The pulsed-flow tests show that the ATM-10 and the CUA glasses leach less rapidly than does the CTS glass. Some MCC data for pulsed-flow tests, in deionized water, are shown in Figures 1 and 2 (MCC monthly August, 1987 report). The increased release rates of the CTS glass over ATM-10 and the CUA glass is evident in the comparison of these figures. The ordinate in Figures 1 through 3 represents the amount of ions released with respect to the total amount in the glass.

Data for Si release from MCC-1 tests in deionized water at 90°C for the CTS, ATM-10 and CUA glasses are shown in Figure 3 (MCC monthly report, Sept., 1987, Fig. 4). Again, the release rate for the CTS glass is much higher. MCC data for B and Na also show increased release of these elements for the CTS glass.

The CTS glass is less durable than either the ATM-10 or the CUA glass. The major compositional differences between the ATM-10 and the CUA glasses are in the silica and alumina contents. The ATM-10 glass has 45.1 percent silica and 6.5 percent alumina. The CUA glass has 40.9 percent silica and 10.2 percent alumina. The ATM-10 and CUA glasses can be considered to be similar. The CTS glass composition differs from the ATM-10 and CUA by containing a decreased silica plus alumina content and an increased boron plus alkali content. These compositional differences result in decreased durability for the CTS glass.

MCC-3 testing of ATM-10 glass in PBB1 brine was conducted. In modified MCC-3 testing which excluded CO_2, release of Th and U were dramatically decreased. All MCC-3 testing was completed, and a summary report was issued. MCC-1 testing of CUA glass in deionized water at 90°C was completed.

Final revisions of the report on ATM-10 are in progress. The characterization of ATM-WV/205 was completed. Results show that this glass meets all target specifications, that the glass is satisfactory for use as a testing material, and ATM/WV-205 is physically similar to ATM-10.

Preparation of a reference West Valley waste glass, using actual waste to replace the actinide-doped glass, is being planned. Due to the high level of radiation expected, this process will be done in a hot cell. Nuclear waste products must be transferred to PNL and initial prechemistry completed before the glass can be produced.

The computerized database is a multifunded task supported at present by the WVDP and the DHLWTP. The purpose of this database is to compile data on material properties. This information is needed by nuclear waste glass producers, the repositories, and other participants in the waste licensing process. The outline for the database was given in previous report [Interrante et al. 1987c, p. 22].

The database was switched from the RS-1 language to the Lotus 1-2-3 spreadsheet. Documentation of the switch was made for QA software control procedures. The first installment of the NBS/NRC directory of nuclear waste data has been received. The format for the computerized database was changed to incorporate comments. The spreadsheet consists of 1400 lines, 76 column headings for each line.

6.10 Comments

The monthly reports of the MCC indicate that the center is responsive to the offices which support it, and the center places emphasis on quality assurance. The MCC monthly reports over the past one and one-half years show considerable progress on test development work for glass leaching and also for materials durability in SRP and BWIP repository environments. MCC has done very little test method development work for the NNWSI repository site.

The test method approval procedure, mentioned in the introductory paragraph of this report, will change and will not involve the MRB in the future. The MRB has been discontinued. DOE materials steering committee has decided to have peer review replace the MRB review of test methods and data. Additional details on approval of test methods and data should be available at a later time.

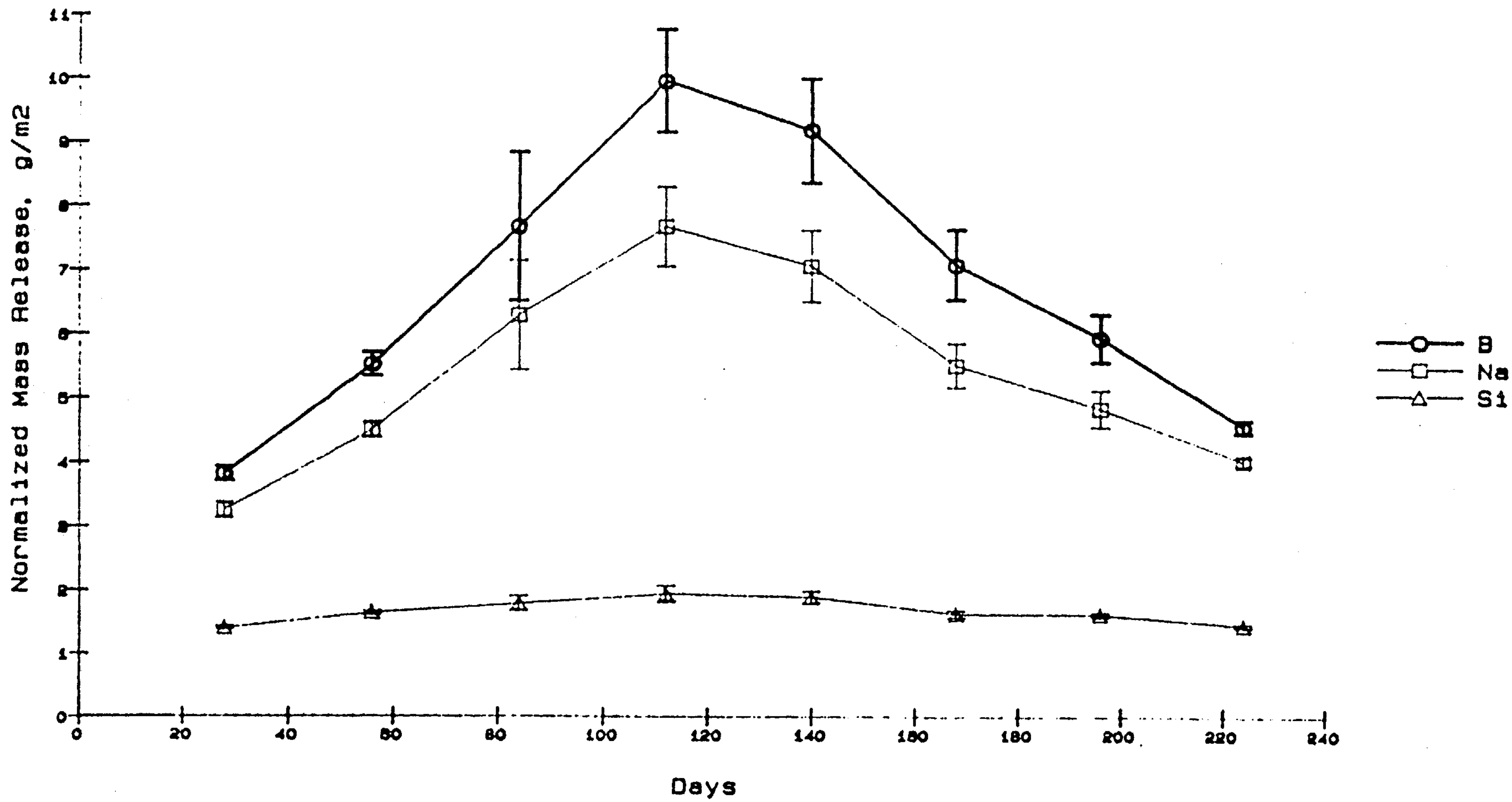

FIGURE 1. Normalized Release of B, Na, and Si from CTS Glass, Pulsed-Flow Test, DIW, 90°C

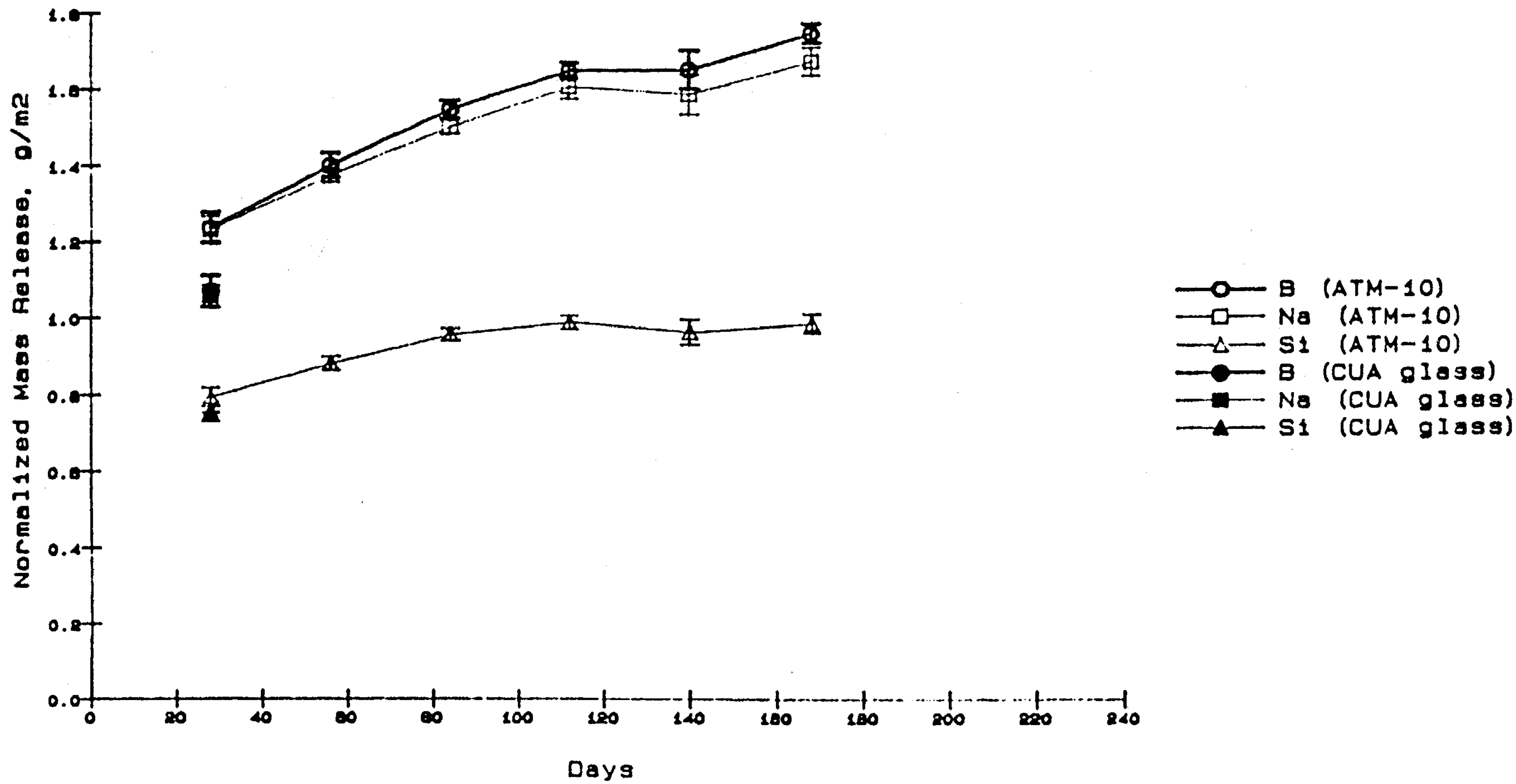

FIGURE 2. Normalized Mass Release of B, Na, and Si from ATM-10 and CUA Glass, Pulsed-Flow Tests, DIW, 90°C

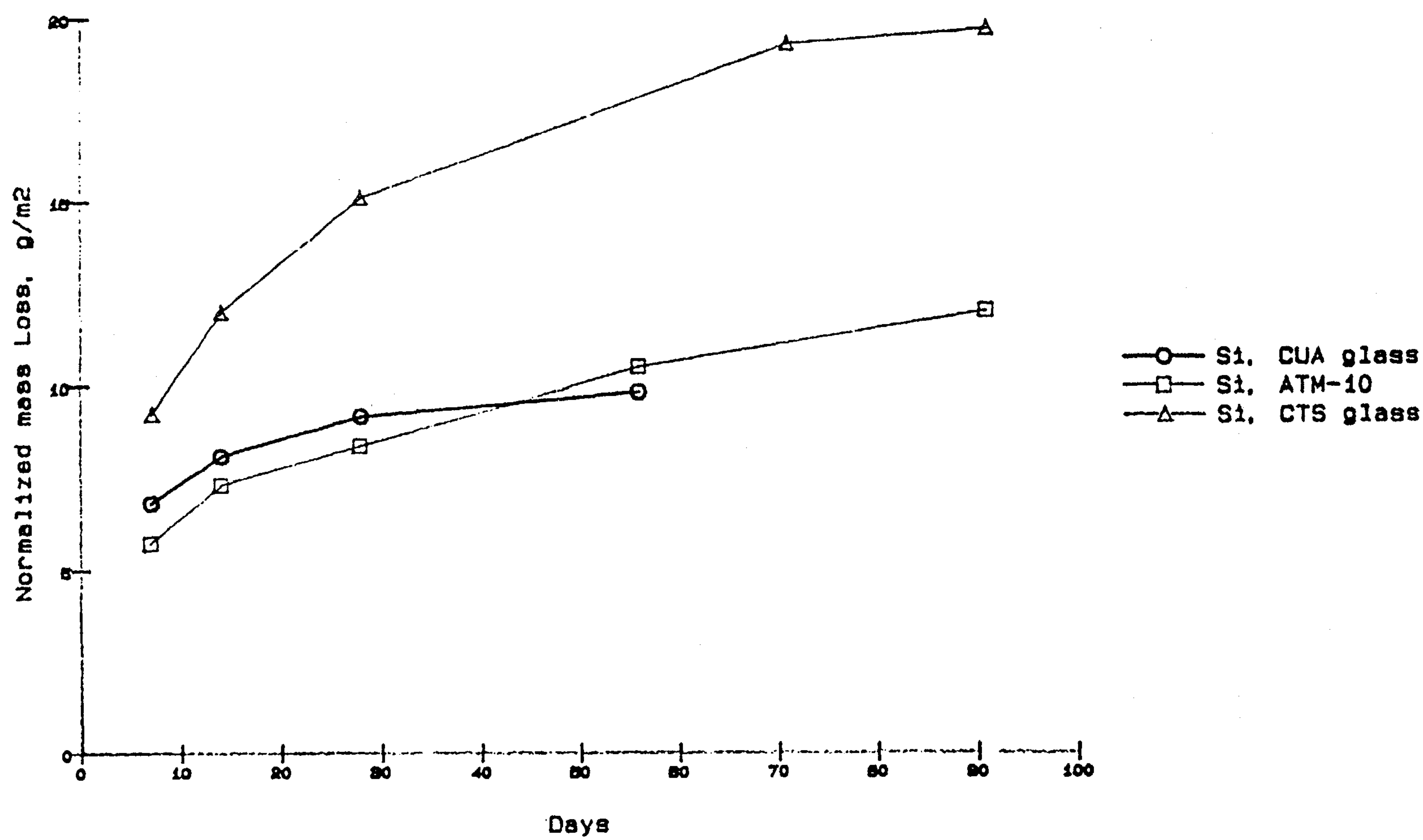

FIGURE 3. Normalized Release of Si from CTS, CUA, and ATM-10
MCC-1, DIW, 90°C

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Appendix A. NBS Reviews and Guidelines for Reviewers of DOE Reports Concerning the Durability of Proposed Packages for High-Level Radioactive Waste

Appendix A. NBS Reviews and Guidelines for Reviewers of DOE Reports Concerning the Durability of Proposed Packages for High-Level Radioactive Wastes

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SRP -- SALT REPOSITORY PROJECT

VITRIFICATION OF HIGH-LEVEL WASTE

Page

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

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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 annealled 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 <u>stated by the author</u>. This also includes qualitative statements by the author on the <u>reliability</u> 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.

KEY WORDS

These are to be checked off on the keyword 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 keyword list.

GENERAL 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 statments, 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; THIS SECTION IS NOT TO BE FILLED IN BY THE REVIEWER AS THE PROGRAM MANAGER ASSIGNS THIS TASK TO A LEAD WORKER.

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.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 20439.

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

Bates, J. K. and Gerding, T. J., "NNWSI Waste Form Test Method for Unsaturated Disposal Conditions," UCRL-15723, SANL 410-001, March 1985. Available from NTIS.

DATE REVIEWED: 3/5/87; Revised 8/21/87; 10/2/87.

TYPE OF DATA

Leach test of waste forms which simulates unsaturated conditions and comparison of results with parametric and analog leach experiments.

MATERIALS/COMPONENTS

J-13 well water preequilibrated with Topopah Spring tuff for 2 weeks at 90°C (also referred to as EJ-13 water), type 304L stainless steel, Savannah River Laboratory 165 (SRL-165) glass frit doped with U, Cs, and Sr. In the analog tests DWPF glass spiked with ^{133}Ba, ^{137}Cs, and ^{152}Eu; teflon®, J-13 water, tuff and 304L stainless steel.

TEST CONDITIONS

These tests are designed to simulate the interaction of the waste form with groundwater in an unsaturated repository. The waste package assemblage consisting of the waste form and the waste form holder is contacted intermittently by dripping J-13 water, which has been preequilibrated with tuff at 90°C. The test temperature is 90°C. The nature and degree of radionuclide release is determined by collection and analysis of the water, and by surface analysis of the assemblage components. The parametric test is identical to the unsaturated test except for the use of a Teflon® container and use of Teflon® rather than the stainless steel waste-form holder.

In the analog leach test the cylindrical spiked DWPF waste package is supported by a stainless steel waste-form holder contained in a cavity in a tuff rock core. The core tuff is separated from the stainless steel support cylinder by a Teflon® sleeve and end caps containing small concentric holes for introduction and removal of water. The space between the sleeve and end caps and the stainless steel cylinder is pressurized against the tuff by water at 1600 psi. Water is forced through the tuff at a small (perhaps 0.1 ml/h) flow rate and collected in a vented container for analysis.

METHODS OF DATA COLLECTION/ANALYSIS

Analysis of leachate by Inductively Coupled Plasma (ICP) spectroscopy, except for uranium which was done by fluorescence. Visual observations of waste forms and containment vessels were made as an indication of how and where interactions occur. Photomicrographs of surface and deposits. Analysis of leachate from DWPF glass was done by gamma counting.

AMOUNT OF DATA

Tables

1. Composition of SRL 165 Glass Used in the Unsaturated Test.
2. Solution Analysis for the NNWSI Unsaturated Test.
3. Concentration of Elements in Water Contained in the Tuff Cup.
4. Component Weight Changes in NNWSI Unsaturated Tests.
5. Parametric Test Results. Duration, wt change, Total Elemental Release for B, Ca, Fe, Li, Mg, Na, Si, and U.

Figures

1. Test Apparatus Used for NNWSI Unsaturated Testing. Figures 2-7 contain six photomicrographs showing changes in stainless steel and deposits formed on glass and stainless steel.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

Primary questions concern different interactions which may occur in laboratory tests, but may not be present in a repository environment. For example, interactions between the waste package and overpack material are not considered in the laboratory experiments.

KEY WORDS

Data analysis, experimental data, leach studies, microscopy, SEM, ICP spectroscopy, gamma counting, laboratory, air, J-13 water, tuff, Teflon®, SRL 165 glass, DWPF glass, high temperature, basic, dynamic, 304L stainless steel, ^{137}Cs, ^{133}Ba, ^{152}Eu.

GENERAL COMMENTS OF REVIEWER

The report gives preliminary data on three types of leach tests. The NNWSI unsaturated leach test simulates conditions expected in the NNWSI repository after the 300/1000 y containment period. Parametric tests are used to study process parameters and in this report were used for the elimination of interaction with stainless steel, groundwater, and the waste package by using a Teflon® container and waste package support rather than stainless steel. The analog test attempts to more closely simulate anticipated repository conditions and is necessary because some of the constraints required in the unsaturated test procedure may not exist in a repository. The authors of the report do not explicitly describe what these constraints are. The unsaturated test method and the parametric method inject droplets of groundwater at prescribed intervals to simulate dripping onto the waste package. In the analog test, water is forced through the tuff at a sufficient pressure to obtain a flow rate of perhaps 1 ml/h. The ANL-85-41 report is a more complete discussion of the unsaturated test on SRL-165 glass and ANL-84-81 is a more complete report of the analog test. Observations include (1) reaction of sensitized stainless steel with the waste form and groundwater in the unsaturated test, and (2) the weight gain of the waste form in the parametric test resulting from the extraction of Ca, Mg, and Si from the J-13 water. The analog test results indicated that most of the ^{133}Ba was associated with the top and bottom sections of the waste form support (stainless steel) with about 30 percent on the bottom tuff, 98 percent of the ^{152}Eu was associated with the stainless steel, and 2 percent with the tuff. The ^{137}Cs was found mainly in the bottom tuff. These distributions were determined by gamma counting techniques.

Comparison of the unsaturated test results with the parametric results indicates that interaction of waste form with stainless steel has been an important factor in these tests while the analog results are not comparable because they involve a different waste form. The volume of the leachate is an important parameter in leach measurements but the data obtained by the procedures used in these experiments appear to be quite uncertain with respect to the volume of leachate in contact with the waste form. This is a serious flaw in this experimental method.

RELATED HLW REPORTS

1. Bates, J. K. and Gerding, T. J., "One-Year Results of the NNWSI Unsaturated Test Procedure: SRL 165 Glass Application," ANL-85-41, January 1985.
2. Bates, J. K. and Gerding, T. J., "NNWSI Phase II Materials Interaction Test Procedure and Preliminary Results," ANL-84-81, January 1985.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues 2.3, concerning when, how and at what rate radionuclides will be released from the waste form.

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

A test method has been developed to measure the release of radionuclides from the waste package under simulated NNWSI repository conditions, and to provide information concerning materials interactions that may occur in the repository. Data are presented from unsaturated testing of simulated Savannah River Laboratory 165 glass completed through 26 weeks. The relationship between these results and those from parametric and analog testing are described. The data indicate that the waste form test is capable of producing consistent, reproducible results that will be useful in evaluating the role of the waste package in the long-term performance of the repository.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA.

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

McCright, R. D., Weiss, H., Juhas, M. C. and Logan, R. W., "Selection of Candidate Canister Materials For High-Level Nuclear Waste Containment in a Tuff Repository, UCRL-89988, April 1984. Available from NTIS.

DATE REVIEWED: 9/30/87.

TYPE OF DATA

1) Experimental
2) General corrosion, localized corrosion, stress corrosion.

MATERIALS/COMPONENTS

AISI Types 304L, 316L, 317L, 321, 409, and 416; Alloy 825, 2.25Cr - 1Mo alloy steel, 9Cr - 1Mo alloy steel, C1020 carbon steel, C1025 carbon steel, A36 carbon steel, A366 carbon steel.

TEST CONDITIONS

1) a. As received - all materials
   b. Sensitized - 304L
   c. Annealed - 304L
2) Rectangular 1 x 2 in coupons
3) a. Tuff Conditioned J-13 Water at 50, 70, 80, 90, 100, and 150°C.
   b. J-13 Water and Tuff conditioned J-13 Water at 105°C with 3 x 10^5 rd/h, and at 150°C with 6 x 10^5 rd/h.
   c. Steam above J-13 water.

METHOD OF DATA COLLECTION/ANALYSIS

1) Electrochemical polarization tests include Tafel slope extrapolation, linear polarization resistance measurements for determining corrosion rates, cyclic anodic polarization scanning for indications related to pitting and crevice corrosion.
2) Slow strain rate and four-point bent beam techniques for stress corrosion testing. Gravimetric weight loss measurements for determining corrosion rates.

AMOUNT OF DATA

Eight tables

Table 1. chemical composition of welded tuff (%);
Table 2. chemical composition of J-13 water (mg/l);
Table 3. dimensions and power output of waste packages (cm, kW);
Table 4. chemical composition of J-13 water expected at 90 and 100°C (mg/l);
Table 5. chemical composition of reference alloy and four alternative canister materials (wt.%);
Table 6. results of coupon corrosion tests for three carbon steels, two alloy steels, and five stainless steels in conditioned J-13 water at 100°C and steam at 100°C (μm/y and visual description of surface);
Table 7. results of coupon corrosion tests in two gamma radiation levels (3 and 6 x 10^5 rd/h) for C1025 carbon steel, 9Cr-1Mo alloy steel, annealed 304L stainless steel, and sensitized 304L stainless steel (μm/y);
Table 8. results of slow-strain-rate tests of annealed 304L and sensitized 304L in J-13 water, steam, and air (strain rate, elongation, reduction in area, yield stress, ultimate tensile stress, and results).

Eight figures

Figure 1. stratigraphic section on Nevada tuff (surface to 750 m below surface);
Figure 2. temperature(0-300°C)-time(0-300 y) of canister surface for different packages;
Figure 3. (initial exposure) and 4(after 500 h), electrochemical determination of corrosion currents(0-1600 nA/cm2) and corrosion rates(μm/y) for different alloys in J-13 water at 100°C;

Figures 5 - 8. corrosion and protection potentials(-600 to +600 mV vs SCE) for 304L, 316L stainless steels, 321 and 825 alloy steels in tuff conditioned J -13 water at different temperatures(40-100°C).

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

The authors acknowledge that these are preliminary results based on short-term exposure times (max. 2 months).

Not discussed.

KEY WORDS

Experimental data, electrochemical, simulated field, Yucca Mountain, J-13 water, air, tuff composition, gamma radiation field, ambient temperature, high temperature, ambient pressure, nickel base, stainless steel, steel, 304L stainless steel, 316L stainless steel, 321 stainless steel, 1020 carbon steel, 1025 carbon steel, high-nickel alloy 825, annealed, sensitized, slow strain rate, four-point bent beam, J-13 steam, tuff, corrosion (crevice), corrosion (general), corrosion (stress cracking) SCC, sensitization.

GENERAL COMMENTS OF REVIEWER

This report describes initial results of corrosion studies on alloys being considered as possible canister or canister-liner materials. The longest exposure time in any given environment is 2 months. The slow-strain-rate results on annealed 304L and sensitized 304L stainless steel in J-13 water did not reveal any susceptibility to stress corrosion failure. Future tests in water vapor may reveal a more aggressive environment.

The 1000-h coupon tests revealed no evidence of localized attack for the stainless steels and the 9Cr-1Mo alloy steel, but there was considerable attack on all the carbon steels and the 2.25Cr-1Mo alloy.

In a gamma radiation field, the 304L stainless steel and the 9Cr-1Mo alloy steel had higher rates of corrosion than similar specimens not irradiated.

These preliminary data indicate that the test procedures are reasonable, but longer exposures and more data are needed before any conclusions can be drawn.

Authors do not describe the model used to define deleterious sensitized structures and the relationship to time/temperature exposures during the anticipated glass pouring heat cycle, environmental thermal cycle, and candidate welding processes. Sensitization corrosion tests should relate the effects of well-defined metallurgical structures. The electrochemical tests selected provide indications of susceptibility to initiation of pitting and crevice corrosion, but do not provide any indications of critical penetration rates.

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

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

Related to NNWSI ISTP issues 2.2.4, the potential corrosion failure modes for the waste package container, and 2.2.4.2, the effects of radiation on the corrosion failure modes and associated corrosion rates for the waste package container.

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

A repository located at Yucca Mountain at the Nevada Test Site is a potential site for permanent geological disposal of high level nuclear waste. The repository can be located in a horizon in welded tuff, a volcanic rock, which is above the static water level at this site. The environmental conditions in this unsaturated zone are expected to be air and water vapor dominated for much of the containment period. Type 304L stainless steel is the reference material for fabricating canisters to contain the solid high-level wastes. Alternative stainless alloys are considered because of possible susceptibility of 304L to localized and stress forms of corrosion. For the reprocessed glass wastes, the canisters serve as the recipient for pouring the glass with the result that a sensitized microstructure may develop because of the times at elevated temperatures. Corrosion testing of the reference and alternative materials have begun in a tuff-conditioned water and steam environments.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Lawrence Livermore National Laboratory, Livermore, CA.

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

Ebert, W. L., Bates, J. K., Gerding, T. J., and Van Konynenburg, R. A., "The Effects of Gamma Radiation on Groundwater Chemistry and Glass Reaction in a Saturated Tuff Environment," UCRL-95884, December 1986. Available from NTIS.

DATE REVIEWED: 8/1/87; Revised 10/31/87.

TYPE OF DATA

(1) Scope of the Report

Laboratory study conducted to measure the effect of penetrating gamma radiation on (1) the groundwater chemistry and (2) the interaction of waste glass components with the components of the tuff repository.

The purpose of these experiments is to produce data applicable to projecting the release of radionuclides from the waste glass and to determine if radiation produces measurable effects on the chemistry of the groundwater or on the glass performance.

(2) Failure Mode or Phenomenon Studied

The leaching of radionuclides from waste glass, due to gamma-radiation-enhanced changes in both the glass and in the groundwater.

MATERIALS/COMPONENTS

Synthetic waste glass, i.e. two compositions of doped SRL 165.

TEST CONDITIONS

(1) State of the Material being Tested

Two synthetic waste glasses based on the composition of Savannah River Laboratory (SRL) 165 black frit were used in the tests. One glass was doped with uranium, cesium, and strontium (SRL U glass), and the other glass was doped with the U, Cs, and Sr and also with ^{237}Np, ^{239}Pu, and ^{241}Am (SRL A glass).

(2) Specimen Preparation

Disks of the waste glass were made with surface areas of about 2.5 cm^2 [no other dimensions are given or needed for leaching calculations].

(3) Environment of the Material being Tested

The leachant used (referred to as EJ-13 water) consisted of Nevada Nuclear Waste Storage Investigations (NNWSI) groundwater that had been prereacted with pulverized tuff at 90°C for 14 days. The test vessel also contained a wafer of Topopah Spring tuff with a surface area about 10 cm^2.

METHODS OF DATA COLLECTION/ANALYSIS

For each experiment, two disks of synthetic waste glass with a wafer of tuff were placed in a 304L stainless steel vessel. The EJ-13 water was added in such a volume as to maintain a gas-to-leachant volume ratio near 0.3 and a glass-surface area to leachant volume near 0.3 cm^{-1}. Vessels were sealed using silicone rubber gasket and compression fittings. Some experiments were carried out using only the EJ-13 water (and no glass) to determine the effects of radiation on the groundwater alone.

All experiments were run in duplicate, both with and without a tuff wafer, and with and without irradiation. The irradiated experiments were run in a 90°C oven in the gamma-radiation facility at Argonne National Laboratory (ANL). The gamma-radiation facility includes a retractable ^{60}Co source. The radiation dose was controlled to 1 x 10^3 Roentgens (R)/h. The nonirradiated experiments were run in a 90°C oven in the laboratory. Exposure times varied from 14 to 280 days; six to seven exposure times were used.

At the end of the exposure, the vessel was cooled to near room temperature before opening. The analysis of the contents included analyzing the leachate pH, the concentration of various anions (ion chromatography), cations (ICP and fluorescence), and released dopants (α-counting). Total dissolved carbon and organic carbon were also analyzed. Glass disks were measured for weight change. The reacted surfaces of the glasses were analyzed using various surface analytical techniques, including SEM/EDS, SIMS, NRS, AES, XPS, and ion microprobe. The tuff surfaces were analyzed in the same ways. Actinides on the glass or tuff specimens were detected by the surface analyses.

Released actinides may not only dissolve into solution, but may also adhere to colloidal material in the leachate, to the vessel surfaces, and to the glass or tuff surfaces. Actinides remaining in the vessels in the leachate or adsorbed on the vessel surfaces, therefore, had to be detected. An aliquot of the leachate was analyzed without treatment and was referred to as "unfiltered". A second aliquot was filtered through a 50Å. The leachate and the filtrate were analyzed for dissolved actinides. A third aliquot was acidified to a pH near 1 with HNO_3, and allowed to stand in the vessel for about 20 hours at 90°C. This procedure dissolved all pseudo-colloidal and adsorbed actinides. This acid-washed solution represents the total amount of actinides.

AMOUNT OF DATA

There are seven figures. Except for figure 3, each contains more than one plot, each of these is identified by (a), (b), etc., in the figure titles.

Figure 1-- "Leachate pH values for experiments performed with (a) EJ-13 only, (b) EJ-13 + SRL U glass: without tuff at 0 rd/h; with tuff at 0 rd/h; without tuff at 1E3 rd/h; with tuff at 1E3 rd/h, plotted vs reaction time." The pH values range from 5 to 9+ for test durations of up to 300 days.

Figure 2-- "Normalized elemental mass losses for (a) boron, (b) lithium, (c) sodium, (d) silicon, and (e) uranium plotted vs reaction time for experiments with EJ-13 + SRL U glass: without tuff at 0 rd/h; with tuff at 0 rd/h; without tuff at 1E3 rd/h; and with tuff at 1E3 rd/h." The normalized elemental mass losses range from 0 to 10 g/m^2 for test durations of up to 300 days.

Figure 3-- "Normalized weight loss of EJ-13 + SRL U experiments: without tuff at 0 rd/h; with tuff at 0 rd/h; without tuff at 1E3 rd/h; and with tuff at 1E3 rd/h plotted vs reaction time." The normalized weight loss ranges from 0 to 10 g/m^2 for test durations up to 300 days.

Figure 4-- "Mass of plutonium in the unfiltered aliquot of experiments: without tuff and with tuff and the mass of plutonium in the acid-washed solution of experiments: without tuff and with tuff irradiated at (a) 1E3 rd/h and (b) 0 rd/h plotted vs the reaction time." The mass of plutonium ranges from 0 to 5 micrograms for test durations of up to 300 days.

Figure 5-- "Leachate pH values for experiments (a) with EJ-13 only, and (b) with EJ-13 + SRL A glass plotted vs the log of the total exposure dose for reactions times of: 28 days; 56 days; 91 days; 181 days; and 278 days. Nonirradiated experiments are plotted at log total dose value of zero for convenience. The diagonal lines represent the amount of H^+ expected to be produced in the vessels from the equation of Burns, et al. The horizontal lines at pH 6.4 represent the pK_a of the CO_2/HNO_3^- buffer at 90°C." The pH ranges from 6 to 9+ and the log of the total dose (R) ranges from 0 to 10.

Figure 6-- "Normalized weight loss of SRL A glasses reacted with EJ-13 (a) with tuff, and (b) without tuff irradiated at: 2E5 rd/h; 1E4 rd/h; 1E3 rd/h; and 0 rd/h plotted vs the reaction time." The normalized weight loss ranges from 0 to 7 g/m^2 for test durations of up to 300 days.

Figure 7-- "Plot of log of the ratio of the "acid washed" and "unfiltered" plutonium fractions vs reaction time for EJ-13 +SRL A experiments irradiated at: 2E5 rd/h; 1E4 rd/h; 1E3 rd/h; and 0 rd/h (a) with tuff and (b) without tuff.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

The experimental design incorporated many of the components expected to be present in a tuff rock repository, but was not intended to simulate predicted repository conditions. Differences between these experimental conditions and the actual repository are given in the following partial list: (1) the gamma field in the repository will be much weaker, only a few rd/h in 1000 years after emplacement, (2) the repository is an open system allowing interchange of gas and groundwater, (3) the ratio of gas to liquid will be substantially greater in the repository, and (4) the amount of tuff surface contacting the groundwater, air, glass, and steel will be much greater in the repository. [Ed. It is not clear to the reviewer that the tuff surface will contact the glass waste form]. Point (3) will allow the pH to become very acidic in small droplets of groundwater, and the amount of bicarbonate may be insufficient to buffer the solution. Point (4) may have a significant effect on the removal of adsorbable species from the groundwater and release of materials into the groundwater by the tuff rock.

KEY WORDS

Experimental data, weight change, chemical analysis, ion chromatography, ICP and fluorescence alpha-counting analyzed, SEM/EDS, SIMS, NRS, AES, XPS, ion microprobe, EJ-13 water, tuff, gamma radiation field, high temperature, ambient pressure, static (no flow), leaching (radiation enhancement).

GENERAL COMMENTS OF REVIEWER

The author refers to experiments (similar to those reported here) performed on other glasses, designated only as ATM-1c and ATM-8 (with no other identification or description). The purpose of these additional experiments was to verify that any radiation effects were not specific to the SRL 165 type glasses. The authors state that the results will be reported elsewhere, but no reference is given for that report.

Although the experiments did not simulate repository conditions, the results of these tests, according to the authors, will be used in the design of more "repository-relevant" experiments.

The results indicate that (1) the major effect of radiation is to lower the groundwater pH to a value near 6.4 due to nitrogen fixation, (2) the reaction of the glass is not strongly influenced by gamma radiation as indicated by leachate concentration measurements, and (3) plutonium may exist as a pseudo-colloid susceptible to being transported away from the near-field environment.

RELATED HLW REPORTS

1. Bates, J. K., Fischer, D. F., and Gerding, T. J., "Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment. Part 1. SRL 165 Glass," ANL-85-62, February 1986.

2. Van Konynenburg, R. A., "Radiation Chemical Effects in Experiments to Study the Reaction of Glass in an Environment of Gamma-Irradiated Air, Groundwater, and Tuff," UCRL-53719, May 1986.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues 2.3.2.2, What non-radioactive dissolution products are likely to be produced from the waste form? 2.3.3.2, How may radionuclides that are released from the waste form will be transported in colloids or in some other suspended particle form?

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

The Nevada Nuclear Waste Storage Investigations project has completed a series of experiments that provide insight into groundwater chemistry and glass waste form performance in the presence of a gamma radiation field at 90°C. Results from experiments done at 1×10^3 and 0 rd/h are presented and compared to similar experiments done at 2×10^5 and 1×10^4 rd/h. The major effect of radiation is to lower the groundwater pH to a value near 6.4. The addition of glass to the system results in slightly more basic final pH, both in the presence and absence of radiation. However, there is essentially no difference in the extent of glass reaction, as measured by elemental release, as a function of dose rate or total dose, for reaction periods up to 278 days.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA.

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

Yunker, W. H. and Glass, R. S., "Long-Term Corrosion Behavior of Copper-Base Materials in a Gamma-Irradiated Environment," UCRL-94500, December 1986. Available from NTIS.

DATE REVIEWED: 9/30/87; Revised 12/14/87.

TYPE OF DATA

Experimental.

MATERIALS/COMPONENTS

Corrosion Development Association (CDA) Copper-base alloy designations, CDA 101, CDA 113, CDA 715

TEST CONDITIONS

Air-water at 150°C; liquid J-13 well water at 95°C; water vapor saturated air phase at 95°C; γ-field 10^5 rd/h

METHODS OF DATA COLLECTION/ANALYSIS

Weight loss; surface composition profiles; auger electron spectroscopy (AES); x-ray spectra of surface phases

AMOUNT OF DATA

Tables

1. Nominal Compositions of Corrosion Specimens (CDA 101, CDA 613, CDA 715)
2. Gas Compositions at 95°C [absolute atmospheres (kPa)]
3. Water Compositions at 95°C
4. Weight Loss and Uniform Corrosion Rates
5. Stoichiometry Estimates of Cu_xO
6. Summary of XRD Analyses

Figures

1. Three Specimen Cages Stacked as in a Corrosion Vessel.
2. Schematic of Corrosion Vessel.
3. Weight Loss vs Time for CDA 101, Pure Copper Specimens.
4. Weight Loss vs Time for CDA 613, Aluminum Bronze Specimens.
5. Weight Loss vs Time for CDA 715, Nickel-Copper Specimens
6. Concentration (atom percent) Profile of the Oxide Layer on CDA 613 Specimen After One Month in the Gas Phase at 150°C. Sputtering rate is the order of 10 nm/min.
7. Concentration (atom percent) Profile of the Oxide Layer on a CDA 715 Specimen After One Month in the Gas Phase at 95°C. Sputtering rate is the order of 10 nm/min.
8. XRD Spectra of CDA 101 Oxide After Three Months at 95°C in Gas Phase. Peak 2 is Cu_2O; peaks marked 1 are CuO; other peaks are Cu.
9. XRD Spectra of CDA 613 in Oxide After Three Months at 95°C in Gas Phase. Peaks marked 3 are Al; peaks marked 1 are CuO; other peaks are Cu.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

Conclusions tentative. Limited testing time (up to 10^4 h for a limited number of tests).

KEY WORDS

Experimental, corrosion, x-ray diffraction, Electron Auger Spectroscopy, laboratory, air, J-13 water, gamma radiation field, ^{60}Co, high temperature, copper base, CDA 101, CDA 613, CDA 715, J-13 water, J-13 steam, corrosion (general), corrosion (pitting), radiation effects.

REVIEWER'S GENERAL COMMENTS

No new data when compared with material presented about eight weeks before (April 1986) at a meeting in Houston, Texas.

RELATED HLW REPORTS

McCright, R. D., "FY 1985 Status Report on Feasibility Assessment of Copper-Base Waste Package Container Materials in a Tuff Repository," UCID-20509, September 1985.

Yunker, W. H., "Corrosion of Copper-Based Materials in Gamma Radiation," HEDL-7612, June 1986. Reviewed by NBS, published in NUREG/CR-4735, Volume 2, page A-37, May 30, 1987.

Acton, C. F. and McCright, R. D., "Feasibility Assessment of Copper-Base Waste Package Container Materials in a Tuff Repository," UCID-20847, September 1986.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

This report addresses NNWSI ISTP issue 2.2.4.2, what are the effects of radiation on the corrosion failure modes and associated corrosion rates for the waste package container?

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

The U.S. Department of Energy is currently evaluating the feasibility of using copper-base materials for the manufacture of nuclear waste containers. One site under consideration for geologic disposal of nuclear waste is at Yucca Mountain, Nevada. One feature of this waste repository will be the initial presence of ionizing gamma radiation at high dose rates, which may alter the corrosive medium. To evaluate such effects, three copper-base materials (pure copper, 7 percent aluminum-copper and 30 percent nickel-copper) have been exposed (presently up to 14 months) to a gamma radiation field of approximately 1×10^5 roentgens/h. The exposure environments have been: (1) both groundwater (regional to the repository site, although taken from a lower elevation) at 95°C, (2) the water-vapor saturated air phase above it, and (3) air/water vapor at 150°C. In addition to uniform corrosion, both pitting and crevice corrosion have been observed.

Characterization of the corrosion layers by X-ray diffraction has shown the presence of mixed copper (I) and copper (II) oxides.

Studies by Auger Electron Spectroscopy (AES) have also been conducted in order to further characterize the compositions and structures of these corrosion products.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

E. I. du Pont de Nemours & Company, Savannah River Laboratory, Aiken, SC 29808.

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

Bibler, N. E., Leaching Fully Radioactive SRP Nuclear Waste Glass in Tuff Groundwater in Stainless Steel Vessels," DP-MS-85-141, May 1986. Available from NTIS.

DATE REVIEWED: 6/19/87; Revised 9/30/87.

TYPE OF DATA

Experimental data, borosilicate glass leaching

MATERIALS/COMPONENTS

Borosilicate glass with Savannah River Plant (SRP) radioactive waste
Borosilicate glass with simulated SRP radioactive waste
Type 316 stainless steel container (Parr reaction vessel)

TEST CONDITIONS

Aqueous environment -- J-13 groundwater with borosilicate glass, 90°C, surface-area-to volume ratio = $100m^{-1}$

METHODS OF DATA COLLECTION/ANALYSIS

Plasma induced spectroscopy
Ion chromatography
Calibrated radionuclide counting techniques

AMOUNT OF DATA

Four tables

(1) Composition of SRP radioactive glass.
(2) Normalized mass losses (g/m^2) for ^{90}Sr and ^{238}Pu for 14 to 134 d exposures in 316 stainless steel containers.
(3,4) Final pH values and concentrations of anions (F^-, Cl^-, NO_2^-, NO_3^-, $SO_4^=$) for leach tests in 316 stainless steel and Teflon® containers.

Three graphs

(1) Normalized mass losses for ^{137}Cs (0 to 5 g/m^2 for 0 to 150 ds) based on tests in Teflon® containers.
(2) Comparison of leaching rates for B, Li, and ^{137}Cs in 316 (0-20 g/m^2) stainless steel and Teflon® (0 to 5 g/m^2) containers for exposures of up to 134 d
(3) Comparison of leaching (0 to 6 g/m^2) rates for B and Li from glass with radioactive and nonradioactive waste, J-13 water, 90°C, approximately 200-d exposure

Twelve references cited

UNCERTAINTIES IN DATA

Data scatter is believed to reflect nonuniform surface finish achieved during remote glass-disc polishing and the presence of insoluble particulates in the nonacidified leachates leading to nonrepresentative sampling.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEYWORDS

Data analysis, experimental data, supporting data, spectroscopy, ion chromatography, laboratory, J-13 water, high temperature, neutral solution (ph = 7), static (no flow), stainless steel, 316 stainless steel, Teflon®, defense high level waste (DHLW), 239Pu, 137Cs, 90Sr, radiation effects.

GENERAL COMMENTS OF REVIEWER

This paper describes leaching rate test procedures used to evaluate the performance of SRP high level nuclear waste borosilicate glass in a tuff environment. Test results are used to substantiate important conclusions regarding interactions between borosilicate glass and the containment vessel proposed for glass waste forms. Type 316 stainless steel containers do not introduce radiolysis effects which the authors previously reported for Teflon®. These effects are attributed to leaching of significant amounts of F^-, Cl^-, NO_2^- and NO_3^- from the Teflon®. The paper also states important conclusions regarding a lack of previously observed radiolysis effects on tuffaceous groundwater (J-13 water at pH 7.4), even in the presence of dissolved air. Similarity of leach rates for radioactive SRP glass and nonradioactive glass with simulated waste are also noted.

A major limitation of the test procedures is the use of the static MCC-1 leach test simulating a water saturated environment. Considerable data scatter was introduced by nonuniform surface finishes on the glass samples which were produced by the remote surface polishing techniques used.

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

(a) Relationship to Waste Package Performance Issues Already Identified

(b) New Licensing Issues

Related to issue 2.3, when, how, and at what rate will radionuclides be released from the waste form?

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

SRP glass containing actual radioactive waste was leached in static tests at 90°C in a tuffaceous groundwater (J-13 water at pH ~7.4) at a SA/V ratio of 100^{m1} in 316 stainless steel vessels. Tests were performed for time periods up to 134 d. Normalized mass losses were calculated for ^{137}Cs, ^{90}Sr, and ^{238}Pu. The ^{137}Cs in the leachate appeared to reach a steady value of ~3 g/m^2, corresponding to a steady-state concentration of only 1.0 ppb for total cesium. The mass losses based on ^{90}Sr and ^{239}Pu appearing in solution were low (<0.3 and <0.01, respectively) because of their low solubilities. However, significant amounts of these radionuclides had deposited on the steel vessel while the amount of deposited ^{137}Cs was negligible. During the leach tests, the pH changed <0.4 units and the only significant effect of radiolysis was reduction of NO_2^-. When compared to earlier tests, the results confirm that leach rates in the earlier tests with radioactive glass in Teflon® (product of Du Pont) vessels were high due to radiolysis of the Teflon®. The results also indicate that radioactive and nonradioactive glasses of comparable composition and surface finish leach essentially identically.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Rockwell International, Richland, WA.

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

Nelson, J. L., Westerman, R. E. and Gerber, F. S., "Irradiation-Corrosion Evaluation of Metals for Nuclear Waste Package Applications in Grande Ronde Basalt Groundwater," RHO-BW-SA-316P, November 1983. Available from NTIS.

DATE REVIEWED: 10/20/87; Revised 12/31/87.

TYPE OF DATA

Experimental; Corrosion; Irradiation-corrosion

MATERIALS/COMPONENTS

Cast ductile iron (ASTM A536, Grade 60-40-8-), 2.5Cr-1Mo cast steel, 1025 cast steel (ASTM 536, Grade 60-30), 1020 wrought steel, Ti-Grade 2, Ti-Grade 12, Specimens in the form of corrosion coupons were used for the iron-base materials. Coupons, U-bend, charpy v-notch and bolt-loaded specimens were used for the titanium materials.

TEST CONDITIONS

General corrosion specimens were exposed in a refreshed autoclave system with synthetic Grande Ronde groundwater sparged with an argon/20 percent oxygen mixture at temperatures of 150 to 250°C with Umtanum basalt present. Irradiation corrosion study specimens were exposed at 250°C in pressure vessels within a water and exposed to gamma radiation (3 x 10^5 rd/h and 2 x 10^6 rd/h) from a Co source. Specimens were exposed from one to three months.

METHODS OF DATA COLLECTION/ANALYSIS

Weight gain, weight loss, X-ray diffraction, and corrosion rate based on penetration divided by total exposure time.

AMOUNT OF DATA

There are three figures and two tables. Figure 1 shows a schematic diagram of the irradiation-corrosion test facility. Figure 2 shows the corrosion rate in $\mu m/y$ vs exposure time in months and is titled "Corrosion of Iron-Base Alloys Exposed to Synthetic Hanford Grande Ronde Basalt Groundwater at 250°C and Co^{60}-irradiation Intensity of 3×10^5 Rd/h." Figure 3 shows hydrogen absorption in Ti-2 and Ti-12 after 10 months exposure to irradiated Grande Ronde basalt groundwater at 250°C. (Increase in hydrogen concentration in mg/L along with a dose rate ranging from 10^4 rd/h to 10^6 rd/h is shown vs the distance from the bottom of the access tube in meters.) Table I gives the composition of Umtanum flow basalt and Table II gives the composition of Grande Ronde Basalt groundwater.

UNCERTAINITIES IN DATA

Corrosion rate data for iron-based alloys exposed for three months in irradiated conditions were higher. This may have been due to the autoclave operating at a slightly elevated temperature and having a vapor phase for several days.

DEFICIENCIES/LIMITATIONS IN DATABASE

More data are needed under conditions more closely simulating the waste package environment.

Corrosion testing of weldments, crevice corrosion data, and studies of environmentally-enhanced fracture are needed.

KEY WORDS

Experimental data, corrosion, irradiation-corrosion test, weight change, x-ray diffraction, laboratory, simulated field, Hanford Reservation, oxygen enriched, basalt composition, simulated groundwater, basalts, gamma radiation field, cobalt 60, high pressure, high temperature, cast steel, cast iron, titanium base, 1020 carbon steel, 1025 carbon steel, Ti-Grade 2, Ti-Grade 12, compact tension, Charpy, v-notch, bolt loading.

GENERAL COMMENTS OF REVIEWER

The purpose of this paper was to study four iron base alloys, titanium-grade 2 alloy, and titanium-grade 12 alloy to determine corrosion resistance under conditions similar to those which nuclear-waste-storage canister conditions. The iron-based materials all showed uniform corrosion (with a corrosion rate 2 to 3 times greater in conditions of irradiation and 250°C than in the absence of radiation.) The highest corrosion rate, 11 $\mu m/y$ (0.43 mil/y or 1.1 cm/1000 y), was observed for the cast iron. The cast iron had some pitting attack, but evidence of pitting was not observed on the other specimens. The cast steel (probably the 1026) showed intergranular attack and some evidence of crevice corrosion. The 2.5Cr-1Mo cast steel had the highest corrosion resistance of the iron-base alloys. This report was written in 1983, and since that time, additional tests involving electrochemical measurements have been conducted.

The results reported in this paper are useful with regard to the simulated environment, the different materials studied, and the types of corrosion shown. The iron-based materials studied did not appear to have sufficient corrosion resistance for long-term use.

The Ti-2 and Ti-12 showed low corrosion rates (calculated to be 0.5 mm in 1000 y for Ti-Grade 2 and 0.3mm in 1000 y for Ti-Grade 12) in both irradiated and unirradiated environments, and showed no evidence of cracking. There was a significant amount of hydrogen absorption; this needs further study. Hydrogen levels of 23 mg/L and 110 mg/L were reported. These values were based on weight gain and the corrosion products formed, and these values could be in error. Failure due to hydrogen embrittlement did not occur in these studies.

RELATED HLW REPORTS

1) Lumsden, J. B., "Pitting Behavior of Low Carbon Steel," SD-BWI-TS-014, August 1985.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues, 2.2.4 potential corrosion failure modes for the waste package container, 2.2.4.1 rates of corrosion as a function of time, 2.2.4.2 effects of radiation on corrosion failure and corrosion rates.

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

The corrosion behavior of several iron-base and titanium-base alloys was studied in synthetic Grande Ronde Basalt groundwater at temperatures of 150°C to 250°C and under irradiation dose rates to 2 x 10^6 rd/h. The objective of these ongoing studies is to help select one or more materials for waste-package canisters that will maintain their integrity for time periods up to 1,000 y in a nuclear waste repository constructed in basalt. The corrosion rates of iron-base alloys under irradiated conditions were generally 2 to 3 times as high as those obtained on similar materials under nonirradiated conditions. The titanium alloys exhibited low corrosion rates but absorbed significant amounts of hydrogen under irradiated conditions.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Rockwell International, Richmond, WA.

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

Salter, P. F., Ames, L. L., and McGarrah, J. E., "The Sorption Behavior of Selected Radionuclides on Columbia River Basalts," RHO-BWI-LD-48, Informal Report, August 1981. Available from NTIS.

DATE REVIEWED: 6/16/87; Revised 10/13/87; 12/31/87.

TYPE OF DATA

Radionuclide distribution coefficients, using a batch-equilibrium technique, have been determined for I, Se, Tc, Sr, Cs, U, Ra, Pu, Am and Np. The effects of temperature, pressure, groundwater composition, and Eh conditions on the distribution coefficient value for these isotopes have been investigated. In addition, sorption isotherms for Cs, Sr, Ra, Pu, and U have been determined.

MATERIALS/COMPONENTS

Radionuclides: I, Se, Tc, Sr, Cs, U, Ra, Pu, Am and Np and basalt.

TEST CONDITIONS

Both oxidation and reduction conditions.

METHODS OF DATA COLLECTION/ANALYSIS

Batch equilibrium technique.

AMOUNT OF DATA

13 Tables and 12 Figures

Tables

1. Synthetic Groundwater Composition.

Figures

11. Freundlich Isotherms, Radium Sorption on Umtanum Basalt.
12. Freundlich Isotherm, Selenium Sorption on Umtanum Basalt.

UNCERTAINTIES IN DATA

1. Selenium is poorly sorbed by basalt at low temperatures (<100°C). At 150°C, the sorption reaction rate may be sufficiently increased to produce a significant removal of Se over the 45 to 60 days experimental period, in spite of increased anion concentrations in the groundwater. Obviously, more data are needed on Se sorption behavior and basalt hydrothermal reaction products before an adequate evaluation of Se sorption at high temperature is possible.

2. Further information on the kinetics of the reduction Se(IV) and the solubility of possible Se compounds is necessary before the behavior of Se in the basalt geohydrologic environment can be adequately understood.

3. The large variation in K and N terms (Fig. 8) between the three basalts is not understood at this time.

4. For Ra and Pu, the Freundlich N constant is greater than one, the isotherm is nonlinear over the concentration range investigated (1E-8 to 1E-12, Ra; 2 to 7E-14, Pu), and a simple Kd value is not a reasonable value to use in calculating a retardation factor.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Experimental data, sorption, laboratory, basalt composition, simulated groundwater, Fe, $Co_3^=$, basalt, ambient temperature, high temperature, ambient pressure, high pressure, basic (alkaline) solution (pH >7), redox condition, static (no flow), ^{237}Np, ^{239}Pu, I, Ic, Sr, Cs, U, Ra, Am, groundwater, sorption behavior.

GENERAL COMMENTS OF REVIEWER

Sorption data of Iodine, Selenium, Technetium, Cesium, Uranium, Radium, Plutonium, Americium and Neptunium on Columbia River basalts has been provided. The behavior of these isotopes under both oxidation and reduction conditions has been investigated. The distribution coefficients and the effects of temperature, pressure, groundwater composition and Eh condition have been determined. The dependence of the radionuclides sorption on their concentrations (sorption isotherms) have been determined for Cesium, Strontium, Radium and Uranium.

The authors conclusion that the Columbia River basalts strongly retard Cesium, Strontium, Radium and Neptunium migration is only relative because of the dependence of the sorption phenomenon on the surface area that will be involved in the process. This conclusion requires further calculation related to available surface area and groundwater flow in the repository site. The data in this paper could be used for further risk evaluation.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), Supporting (X)]

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issue, 3.3.3, what is the importance reaction and sorption kinetics on radionuclide release and transport in the disturbed zone/far field under various flow regimes?

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

The sorption behavior of selected radionuclides on the Columbia River basalts has been investigated. Radionuclide distribution coefficients, using a batch-equilibrium technique, have been determined for iodine, selenium, technetium, strontium, cesium, uranium, radium, plutonium, americium, and neptunium. Since the distribution coefficient value is an empirical value, the effects of temperature, pressure, groundwater composition, and Eh conditions on the distribution coefficient value for these isotopes have been investigated. In addition, sorption isotherms, describing

the dependence of radionuclide sorption on radionuclide concentration for cesium, strontium, radium, plutonium, and uranium (under both oxidizing and reducing conditions) have been determined. Based on these sorption data, it appears that, under the expected ambient repository conditions (e.g., reducing, alkaline conditions), the Columbia River basalts are capable of strongly retarding cesium, strontium, radium, and neptunium migration and moderately retarding uranium, technetium, and plutonium migration. The basalts are not capable of significantly retarding the migration of iodine and selenium.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Rockwell International, Rockwell Hanford Operations, P. O. Box 800, Richland, WA 99352.

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

Halko, D. J., "Determination of Dissolved Gases in Basalt Groundwater in the Pasco Basin, Washington," Basalt Waste Isolation Project, RHO-BW-SA-554P, September 1986. Available from NTIS.

DATE REVIEWED: 11/19/87; Revised 12/4/87.

TYPE OF DATA

Analytical, sampling techniques - The paper describes sampling techniques for dissolved gases in groundwater and chromatographic analytical procedures for determining amounts of argon, oxygen, nitrogen, carbon monoxide, carbon dioxide and methane present. One table of data is given as an example of how the method works.

MATERIALS/COMPONENTS

Gases dissolved in groundwater including argon, oxygen, nitrogen, carbon monoxide, carbon dioxide and methane and purged gases from solution are analyzed by a gas chromatographic method. Water in confined and unconfined aquifers in basalt under the Hanford Site in the state of Washington.

TEST CONDITIONS

The gas chromatograph is equipped with thermal conductivity and flame ionization detectors and also uses a purge device. Gas chromatography is conducted on groundwater samples, at ambient temperature and pressure, obtained with a downhole grab sampling device. Water samples taken at the surface are from a gas separator barrel or from a sampling port placed in the pipeline before the gas separator barrel. Gas samples are taken when increased gas flow in the separator is present. A purge device is used to separate gas from the water. A Molecular Sieve 5A column separates argon, oxygen, nitrogen, carbon monoxide and methane, and another column, Porapak q, a porous polymer, separates carbon dioxide, methane and water.

These columns are used in interchangeable sequence and will separate all components. The sequence of column switching is critical and is discussed.

METHODS OF DATA COLLECTION/ANALYSIS

A Varian Model 3400 gas chromatograph is used. Columns packed with active solids, Molecular Sieve 5A and a porous polymer (Porapak q), are used. The gas sample is carried through the columns with ultra high purity helium as the carrier gas. Sample components are separated in the columns and detected with a thermal conductivity detector (TCD) and a flame ionization detector (FID) in series. The TCD and FID which are interfaced with a data system computer (Analytical Model 3000 Chromatography Data System).

AMOUNT OF DATA

Figures

There are 13 figures.

Figure 1 shows the location of the Hanford site.
Figure 2 shows the stratification of the Hanford site.
Figure 3 show the Narrow-diameter grab sampling device.
Figure 4 shows the groundwater sample containers.
Figure 5 shows the gas separator barrel and associated plumbing for well-head gas measurements.
Figure 6 shows basic components of a gas chromatographic system with a purge device.
Figure 7 shows the flow path through columns.
Figure 8 shows Chromatograms of the separation of a gas standard mixture with each component at 5 vol. percent in helium.
Figure 9 is Chromatograms illustrating effect of column sequence reversal timing on component separation-initially, Porapak Q is the first column and Molecular Sieve 5A is the second column, then the sequence is reversed.
Figure 10 shows the purge device and chromatographic system.
Figure 11 shows chromatograms of a calibration standard with each component at 5 percent vol. Helium-timing of column sequence reversal and column isolation are indicated.
Figure 12 is a Chromatogram of gases purged from 9 mL of groundwater collected with a downhole grab sampler.
Figure 13 is a Chromatogram of gases and water purged from groundwater.

Table

There is one table entitled Dissolved gases in groundwater from a confined aquifer 427 m (1400 ft.) below the surface sampled from a gas separator barrel and with a downhole grab sampler.

UNCERTAINITIES IN DATA

There are no data. The author warns that the timing of valve switching from one column to another is critical for assuring that oxygen, carbon and nitrogen enter the Molecular Sieve 5A column and to prevent water from entering and deactivating the Molecular Sieve 5A column. Carbon dioxide (CO_2) and water are retained in the Porapak Q column, and the Molecular Sieve 5A column separates the carbon monoxide, oxygen, nitrogen and methane. Water must not be allowed to enter the Molecular Sieve 5A column.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Hanford Reservation, basalt, groundwater, dissolved gases, oxygen, nitrogen, carbon dioxide, carbon monoxide, methane, ambient temperature, ambient pressure, subambient temperature.

GENERAL COMMENTS OF REVIEWER

The test method as described uses calibration standards. Test data need to be produced and analyzed to determine how well the sampling and analytical methods are working. Both are complicated processes. Sampling procedures must present loss of the dissolved gases and in the analytical procedures, the valve switching controlling the column sequence reversal must be timed properly to assure that oxygen, nitrogen and carbon monoxide enter the Molecular Sieve 5A column for separation. Valve switching and other manipulations must be carried out so that water does not enter and deactivate the Molecular Sieve 5A column. Future reports should tell more about the use of this procedure for determining dissolved gases in basalt groundwater.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues, 2.1.2 regarding physical characteristics of groundwater reaching the waste package container, and 2.1.3 regarding chemical characteristics of groundwater reaching the waste package.

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

The determination of dissolved gases in groundwater is required for complete hydrochemical characterization of the Columbia River Basalt Group beneath the Hanford Site. A gas chromatographic method has been developed for the determination of argon, oxygen, nitrogen, carbon monoxide, carbon dioxide, and methane in groundwater. In addition to a gas chromatograph equipped with thermal conductivity and flame ionization detectors, equipment utilized consists of a purge device that strips these gases from solution for subsequent separation using Molecular Sieve 5A and porous polymer columns. This technique is capable of accommodating pressurized fluid samples collected from the deep aquifers with in situ samplers. The analysis is discussed in detail.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Rockwell Hanford Operations, Westinghouse Hanford Company, and Pacific Northwest Laboratory, Richland, WA.

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

Duncan, D. R., "Feasibility Assessment of Copper-Base Waste Package Container Materials in a Repository in Basalt", SD-BWI-TA-023, September 1986. Available from NTIS.

DATE REVIEWED: 9/21/87; Revised 12/16/87.

TYPE OF DATA

Experimental

MATERIALS/COMPONENTS

OFHC Copper, Cu-10% Ni, P-deoxidized Copper

TEST CONDITIONS

Simulated Basalt environment,

METHODS OF DATA COLLECTION/ANALYSIS

1) Weight loss (Air/steam)
(Flowby autoclave)
(Pressure vessel with and with γ-irradiation)

2) Electrochemical Measurements
   a) Potentiodynamic scans (pitting potential)
   b) Polarization resistance R_p
   c) Open circuit potential E_{oc}
   d) Pit growth tests

3) Environmentally Assisted Cracking
   a) Slow-Strain-Rate Tests
   b) Fracture Mechanics Tests

AMOUNT OF DATA

1) Weight loss

11 Tables giving corrosion rate for 4 environments

a) Air/steam
b) Flowby autoclave
c) Pressure vessel, no γ-radiation
c) Pressure vessel, with γ-radiation

Temperature investigated ranged from 50°C to 300°C, but not for all conditions. Exposure Times ranged from 1 month to 10 months.

2) Electrochemical Measurements

a) Two Figures - Electrode potential vs log c.d.

Two Tables giving electrochemical parameters as a function of temperature and exposure time

b) Four Figures - R_p vs Time and $\int R_p(dt)$ vs Time
c) Two Figures - E_{OC} vs Time
d) One Table - Pit Growth Test Parameters

3) Environmentally Assisted Cracking

a) One Figure - Drawing of Test Assembly
Two Tables - SSR tests results for Cu-10%Ni and OFHC Copper
Four Figures - Fractographs

b) Four Figures - Load vs Displacement Curves
c) One Figure - Load Relaxation: Load vs Time

UNCERTAINTIES IN DATA

Standard deviation given in the weight loss tests.

DEFICIENCIES/LIMITATIONS IN DATABASE

Considered a preliminary survey to test feasibility.

KEY WORDS

Experimental data, corrosion, electromechanical, linear-elastic fracture mechanics (LEFM), microscopy, tensile testing, weight change, simulated field, Hanford Reservation, basalt composition, basalt, bentonite, gamma radiation field, high temperature, copper base, OFHC Copper, 90/10 Cu/Ni, P-deoxidized Copper, slow strain rate, bolt or wedge loading, groundwater.

GENERAL COMMENTS OF REVIEWER

As a general survey the work is reasonably good, but it cannot really support the optimistic view taken in the conclusion.

The real weakness of the uniform corrosion tests lies in the scatter of the data, which is well outside the calculated values of the standard deviation for each test. This to us means that some uncontrolled, but significant factor affects the corrosion rate in a certain run, so that all specimens of the same material in that run corrode at similar rates (hence the relatively small s.d.), but the results can change dramatically in the next run. One is forced to conclude that the results so far obtained are largely meaningless.

Electrochemical tests were not repeated, but one suspects that similar effects would be found on repeated testing. Also, one of the critical issues not yet addressed is how the altered solution chemistry due to γ-radiation will affect these tests.

As far as EAC is concerned, since the mechanism for cracking is not known, and cracking has been observed in several disparate environments, results of the tests performed to date are no reason for optimism.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues 2.2.4, what are the potential corrosion failure modes for the waste package container? and 2.2.4.1, what are the rates of corrosion as a function of time for the various corrosion modes of the waste package container?

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Cortest Columbus, Inc. and Battelle Columbus.

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

Beavers, J. A., Thompson, N. G., Markworth, A. J., "Pit Propagation of Carbon Steel in Groundwater," to be published, Localized Corrosion Conference, National Association of Chemical Engineers (NACE), Orlando, FL, June 1987.

DATE REVIEWED: 10/22/87; Revised 12/31/87.

TYPE OF DATA

Scope: experimental, theoretical modeling
Failure mode studied: pitting, pit propagation

MATERIALS/COMPONENTS

1020 steel waste canister

TEST CONDITIONS

Material: hot-rolled 1020 steel, selected tests with intact millscale
Environments: (1) simulated basalt groundwater, (2) pitting solution containing Fe, Cl, F, Si, CO_3, BO_3, NO_3, Na and SO_4, and (3) synthetic brine developed to promote active corrosion of carbon steel

METHODS OF DATA COLLECTION/ANALYSIS

Electrochemical tests using artificial pits with and without reactive pit walls and theoretical modeling.

AMOUNT OF DATA

Tables

(1) nominal compositions of brine solutions

(2) experimental parameters for pit propagation tests
1:05 to 1:10 pit diameter to depth ratio
two pit-packing solutions (used to stimulate pit initiation)
158 to 312 hour exposures three test solutions (see Test Conditions)
steel samples with and without millscale

(3) composition of 1020 steel

(4) summary of electrochemical pit propagation experiments in simulated basalt groundwater

(5) summary of electrochemical pit propagation experiments in three test solutions

Figures

(1) potentiodynamic polarization curve for 1020 steel in deaerated basalt groundwater at 90°C and a scan rate of 0.6 V/h

(2) pit propagation test schematic

(3) current density as a function of exposure time and pit wall reactivity - simulated aerated basalt groundwater at 25°C

(4) coupled potential as a function of exposure time - simulated aerated basalt groundwater at 25°C

(5) potential as a function of exposure time - simulated aerated basalt groundwater at 25°C

(6) potential of pit along pit wall - simulated aerated basalt groundwater at 25°C

(7) potentiodynamic polarization curve for 1020 steel in deaerated solution #47 (pitting solution) at 90°C and scan rate of 0.6 V/h

(8) current density as a function of exposure time and pit wall reactivity - aerated pitting solution at 25°C

(9) potential of pit along pit wall - aerated pitting solution at 25°C

(10) current density as a function of exposure time and pit wall reactivity - aerated brine stimulating active corrosion

(11) schematic of pit geometry assumed in model used in earlier studies

(12) cation concentration as a function of distance along pit depth - reactive vs nonreactive pit walls

(13) distribution of electrostatic potential along pit length - reactive vs nonreactive pit walls

(14) variation of current density along pit length - reactive vs nonreactive pit walls

(15) schematic showing postulated current behavior for reactive and nonreactive wall pits

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Experimental data, theory, electrochemical, simulated field, laboratory, brine, brine (high ionic content), carbon steel, 1020 carbon steel, hot rolled, corrosion (pitting).

GENERAL COMMENTS OF REVIEWER

This paper describes important studies of factors affecting pit propagation in 1020 steel exposed in 25°C brines. Test data were used to develop theoretical models which indicate marked effects of pit wall reactivity on pit propagation rates. Nonreactive pit walls, as used in many earlier pitting models*, were found to accelerate pit propagation rates. Tests also indicate that environments that promote active corrosion of carbon steel will not support pit propagation even in the presence of a differential aeration or pH cell. Test results are based on a unique pit geometry with pitting initiated through introduction of an agressive pitting solution at the base of an artificial pit. Numerical pitting rate data, calculated from electrochemical data with exposure periods ranging from 158 to 312 hours, should not be used to predict penetration rates for long-term container exposures in repository environments.

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*Author cites the following references.

1. Tester, J. W. and Isaacs, H. C., "Diffusional Effects in Simulated Localized Corrosion", J. Electrochem. Soc., Vol. 122, No. 11, p. 1438 (1975).

2. Pickering, H. W. and Frankenthal, R.P., "On the Mechanism of Localized Corrosion of Iron and Staninless Steel", J. Electrochem. Soc., Vol. 119, No. 10, p. 1297 (1972).
3. Alkire, R., Ernsberger, D., and Damon, J., J. Electrochem. Soc., Vol. 123, No. 4, p. 458 (1976).
4. Gaivele, J. R., "Transport Processes and the Mechanism of Pitting of Metals", J. Electrochem. Soc., Vol. 123, No. 4, p. 464 (1976).

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues 2.2.4, what are the potential corrosion failure modes for the waste package container? and 2.2.4.1, what are the rates of corrosion as a function of time for the various corrosion modes of the waste package container?

(b) New Licensing Issues

(c) General Comments

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Basalt Waste Isolation Progect, Research Laboratory Department, Richland, WA.

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

Lane, D. L., Allen, C. C., and Adee, R. R., "Progress Report on the Hydrothermal Interaction of Defense Waste Glasses with Basalt and Groundwater at 150°C," SD-BWI-TI-312, 12/26/85. Available from NTIS.

DATE REVIEWED: 11/4/87; Revised 12/18/87.

TYPE OF DATA

Experimental data from a series of hydrothermal experiments using SRL-DHLW glasses. Data on the glass behavior under hydrothermal conditions: 150°C and 10MPa for periods up to 6 months.

MATERIALS/COMPONENTS

ATM-9 glass, ATM-11 glass, GR-3 groundwater, GR-4 groundwater, SRL-165 frit.

TEST CONDITIONS

Autoclave tests using groundwater in presence of basalt at 150°C, 10MPa, water/solid mass ratio=10 and basalt/ATM-9 mass ratio=1.

METHODS OF DATA COLLECTION/ANALYSIS

Microprobe analyses, ICP analyses, GEA analyses, Scaning Electron Microscopy(SEM), Dispersive X-ray Spectrometer(EDS), Wavelength Dispersive Spectrometer(WDS), Transmission Electron Microscopy(TEM), X-ray diffraction.

AMOUNT OF DATA

15 tables and 41 figures

Tables

Figures

concentrations are x10^4 while uranium concentrations are x10^2. Error bars represent $\pm$50 percent relative percent uncertainty for ^{99}Tc and ^{239}Pu and $\pm$20 percent for U.

5. Concentration vs time data in the system basalt+ATM-11+GR-3 groundwater at 150°C and 10 MPa (D5-9) showing the effect of filteration. Open circles represent data from unfiltered solution; closed circles are data from 0.4 micron-filtered solution, while open squares are data from 0.4 micron + 30Å-filtered solutions. Error bars represent $\pm$50 relative percent uncertainty for unfiltered and 0.4 micron-filtered solutions and 100 percent for the 0.4 micron + 30Å-filtered solutions. Triangles represent ^{241}Am concentration for 0.4 micron-filtered solutions in the absence of basalt (D10-1) and the arrow indicates concentration at or below detection limits.
6. pH vs time in the systems basalt+ATM-11+GR-3 groundwater (D5-9) and ATM-11+GR-3 groundwater (D10-1) at 150°C and 10 Mpa.
7. Concentration vs time data for Na and B in the systems ATM-11+Gr-3 groundwater (D10-1, large symbols) and basalt+ATM-11+GR-3 groundwater (D5-9, small symbols) at 150°C and 10 Mpa.
8. Percent inventory in solution vs time for the system ATM-11+GR-3 groundwater at 150°C and 10 MPa (D10-1). B, Na, Li, U, and Tc values were derived from 0.4 micron-filtered solutions while Np values represent unfiltered solutions. U and Np symbols with arrows indicate maximum values since solution concentrations were at or below detection limits.
9. Unreacted ATM-9 glass; polished section; location of spectrum in figures 10a and 10b shown by black star. Frame width = 192 microns.

10a. EDS spectrum of unreacted glass ATM-9 glass shown in figure 9. (Linear vertical scale; spectrum 1481)

10b. EDS spectrum of unreacted ATM-9 glass shown in figure 9 (logarithmic vertical scale; spectrum 1481)

11. Unreacted ATM-9 glass. Frame width=194 microns. (photo 1733).

12. Unreacted ATM-11 glass; polished section; location of EDS spectrum in figure 13 shown. Frame width=530 microns. (photo 1703).

13a. EDS spectrum of unreacted ATM-11 glass shown in figure 12; linear vertical scale. (spectrum 1467).

13b. EDS spectrum of unreacted ATM-11 glass shown in figure 12;logarithmic vertical scale. (spectrum 1467).

14a. Altered basalt grain from test D6-23 (834 h duration). Note dissolution textures of mesostasis. Frame width=153 microns. (photo 1663).

14b. Altered basalt grain from test D6-30 (3042 h duration). Note dissolution textures of mesostasis. Frame width=162 microns.(photo 1716).

15. Altered ATM-9 glass from test D6-23. Location of spectra in figures 16a and 16b shows by stars. Frame width=127 microns.(photo 1664).
16a. EDS spectrum of center of altered glass grain in figure 15. (spectrum 1426).
16b. EDS spectrum of tip of altered glass grain in figure 15. (spectrum 1427).
17. Altered ATM-9 glass from test D6-23. Relative concentration histogram for boron along indicated baseline is superimposed. Frame width=149 microns.(photo 1689).
18. Altered ATM-9 glass from test D6-30. Relative concentration histogram for boron along indicated baseline is superimposed. Frame width=272 microns.(photo 1631B).
19. EDS spectrum of center of altered glass grain in figure (spectrum 1383). Comparison with the spectrum in figure 10b of the unreacted glass demonstrates that no significant leaching of major elements occurred.
20a. Altered ATM-9 glass from test D6-30. (3042 h duration). Frame width=207 microns.(photo 1596).
20b. Altered ATM-9 glass from test D6-30. Note the thin alteration rinds. Frame width=74 microns.(photo 1603).
21a. Altered ATM-9 glass from test D6-23. (834 h duration). Frame width=127 microns.(photo 1490).
21b. Altered ATM-9 glass from test D6-23. Frame width=131 microns.(photo 1485).
22. Reaction products on altered ATM-9 glass; detail of figure 21a; location of spectrum in figure 23 shown by star. Frame width = 47 microns. (photo 1491).
23. EDS spectrum of reaction products shown in figure 22. (spectrum 1305). A semi-quantitative stoichiometry corresponds roughly to that of zeolite with a high Si/Al ratio.
24. Reaction products on altered ATM-9 glass; detail of figure 21b; location of spectrum in figure 25 shown by star. Frame width = 49 microns. (photo 1486).
25. EDS spectrum of reaction products shown in figure 24. (test D6-23; spectrum 1303). This is interpreted to be the spectrum of a partially reacted shard of ATM-9.
26. Altered ATM-9 glass from test D6-30. Frame width=290 microns.(photo 1599).
27. Reaction products from test D6-30 interpreted to be zeolite. Detail of figure 26; location of spectrum in figure 28 shown. Frame width = 26 microns. (photo 1601).
28. EDS spectrum of reaction products shown in figure 27. (spectrum 1366).
29. EDS spectrum of glass shard from RA-267, the 40-h filter sample from test D6-30. (spectrum 1430).
30. XRD spectrum of particulates from 40-h, 0.4 micron-filtered sample of D6-30.

31. EDS spectrum of molybdenum-rich particle from 40-h, 0.4 micron-filtered sample of test D6-30. (spectrum 1285).
32. Altered basalt and ATM-11 glass from test D5-9 (4387 h duration); polished section. Note the extensive basalt mesostasis dissolution textures. Frame width = 248 microns. (photo 1641).
33. Altered ATM-11 glass from test D5-9. Frame width = 74 microns. (photo 1635).
34. Altered ATM-11 glass from test D5-6; location of spectrum in figure 35 shown. Frame width = 201 microns. (photo 1652)
35. EDS spectrum of alteration product shown in figure 34. (spectrum 1419) Note similarity to spectra of "zeolites" of D6-23 and D6-30 in figures 23 and 28.
36. XRD spectrum of particulates from 233-h, 0.4 micron-filtered sample of D5-9.(basalt+ATM-11+GR-3 groundwater).
37. EDS spectrum of uranium-rich particle from 4386-h, 0.4 micron-filtered sample of D5-9. (spectrum 1452).
38. Particles from RA-335, the 984-h filter sample from test D10-1 (ATM-11+GR-3 groundwater); location of spectrum in figure 39 shown by star. Frame width = 136 microns. (photo 1680).
39. EDS spectrum of uranium-rich particle shown in figure 38. (spectrum 1440).
40. Altered SRL 131/TDS-3Å glass from test D8-1 (basalt+glass+Gr-3 groundwater at 150°C); polished section; location of spectra in figures 41a and 41b shown by stars. Note the thick alteration layers and the core of essentially unreacted glass. Frame width = 118 microns. (photo 1375).

41a. EDS spectrum of center of glass grain in figure 40. (spectrum 1244)

41b. EDS spectrum of alteration layer on glass grain in figure 40. (spectrum 1245) Note the depletion of Na and Al, and the enrichment in K relative to the spectrum from the glass core in figure 41a.

UNCERTAINTIES IN DATA

An uncertainty of ±10 to ±15 percent of the value determined is assumed for ICP analyses; uncertainties of ±50 percent of the value determined are assumed for plutonium analyses, and ±20 percent of the value determined for the uranium analyses.

DEFICIENCIES/LIMITATIONS IN DATABASE

Few conclusions, if any, can be drawn from ^{237}Np data since all concentrations were values "less than" below the detection limit.

KEY WORDS

Experimental, microscopy, x-ray diffraction, SEM, EDS, WDS, TEM, laboratory, groundwater, basalt, high temperature, high pressure, ^{237}Pu, ^{239}Pu, leaching (radiation enhancement), matrix dissolution (glass).

GENERAL COMMENTS OF REVIEWER

This is a progress report for the Basalt Waste Isolation Project (BWIP). The behavior of borosilicate glass under hydrothermal conditions (150°C, 10MPa) has been studied using surface analyses techniques.

It was found that SRL-165 glass is more durable than SRL-131 glass in the presence of basalt. Hydrothermal reactions in the system SRL-165(ATM-11)+groundwater at 150°C maintain lower pH's than reactions with SRL-131 glass under the same conditions. The concentrations of Am were significantly decreased by filtration through 0.4 micron and 30Å membranes indicating that Am was associated with particulates and/or colloidal material. This effect was observed in both cases (with and without basalt).

Longer duration tests are necessary to determine whether a steady state is achieved and to provide additional data for understanding the long-term behavior of radionuclides. Techniques with better sensitivities for analysis of ^{237}Np in the hydrothermal solution need to be established.
In test D5-9, after 4386 h at 150°C, boron did not reach a steady state, while the data for Li, Na, and Si are open to interpretation. Longer test durations may be needed to address this question.

It is very important to understand the behavior of plutonium, as it is the most hazardous radionuclide in the nuclear waste form. The fact that the behavior of plutonium cannot be explained by the authors shows that more data are necessary for a clear understanding of its behavior.

In all experiments, two parameters were held constant: (1)water/solid mass ratio, and (2)basalt/ATM-9 mass ratio. The most important parameter in such experiments, however, is the surface/volume ratio. This parameter was not only neglected, but also the surface area of the samples was not measured at all.

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, what is the solubility of the waste form under a range of potential repository conditions?

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Westinghouse Hanford Co. for Rockwell Hanford Operations, Richland, WA.

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

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

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

TYPE OF DATA

(1) Scope of the Report

Experimental laboratory data

(2) Failure Mode or Phenomenon Studied

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

MATERIALS/COMPONENTS

ASTM A36 steel plate
ASTM A387 Grade 9 steel plate

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

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

TEST CONDITIONS

(1) State of the Material being Tested

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

(2) Specimen Preparation

Modified wedge-open-loading (MWOL) specimens were used [the proper, ASTM term and symbol, [ASTM E616-82] are "bolt-loaded 1T modified-compact specimens, $MC(W_b)$]." Two figures show the specimens and a table contains the dimensions. Specimens were cyclically precracked in air at room temperature on an MTS electrohydraulic testing machine using load as the control parameter. The fatigue precracks simulated relatively long cracks. Maximum levels of the stress-intensity factor (K) achieved during precracking are given in a table (they were always less than the initial test K-levels which were 30, 40, and 60 $MPa \bullet m^{1/2}$). After precracking, the elastic compliance of each specimen was measured using the load cell of the MTS machine and a clip gage (MTS Model 632.01) seated in the knife edges that were machined into the front face of the specimen. A table in the report gives the precracking conditions. Specimens were loaded initially by using a wrench to torque the specimen loading bolt, while holding the specimen in a vise with the crack pointed downward, until the desired initial crack mouth opening displacement (CMOD) was obtained. Plastic tape was used to "dam" the areas of the notch and the crack, and these areas were filled with simulated Hanford groundwater prior to loading the specimen.

(3) Environment of the Materials Being Tested

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

METHODS OF DATA COLLECTION/ANALYSIS

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

AMOUNT OF DATA

Data for one short-term (about 24 h) and two complete tests (2000 h) are included. There are three tables listing measured and calculated results. Table 8 is titled "Summary of Measured and Calculated Results for Test No. 1 (<24 h at 250-270°C)." Table 9 is titled "Summary of Measured and Calculated Results for Test No. 2 (2180 h at 150°C)." Table 10 is titled "Summary of Measured and Calculated Results for Test No. 3 (2000 h at 250°C)." Each table lists initial and final applied K-levels, initial and final loads, initial and final displacements, plastic and wedged crack mouth opening displacements (V), initial and final compliances, average initial surface crack lengths, predicted initial and final crack lengths, and average final crack length.

The data are for three specimens each of the two steels, and are plotted in six load-displacement diagrams:

Figure 12 is titled "Load-displacement Diagram for A36 Steel Specimens in Test No. 1."
Figure 13 is titled "Load-displacement Diagram for A387-9 Steel Specimens in Test No. 1."
Figure 14 is titled "Load-displacement Diagram for A36 Steel Specimens in Test No. 2."
Figure 15 is titled "Load-displacement Diagram for A387-9 Steel Specimens in Test No. 2."
Figure 16 is titled "Load-displacement Diagram for A36 Steel Specimens in Test No. 3."
Figure 17 is titled "Load-displacement Diagram for A387-9 Steel Specimens in Test No. 3."

The diagrams give the applied K versus V for each of the two steels, for each of the triplicate tests. The K values range from 0 to 60 $MPa \bullet m^{1/2}$ and the V values range from 0 to 0.6 mm.

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

UNCERTAINTIES IN DATA

The load-displacement diagrams for the 24-h test carry the note that P_f and C_f, the final values of load and compliance (deflection divided by load) respectively, were not measured; therefore, the plots are only approximate.

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

DEFICIENCIES/LIMITATIONS IN DATABASE

Because precracking and compliance testing were done in air at stress-intensity factor (K) levels lower than the initial test K levels, the first application of the actual test loads occurred in the presence of the groundwater environment.

Therefore, any dislocation generation, plasticity, or creation of new crack-tip surfaces occurred in the presence of groundwater at ambient conditions.

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

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

An extensive appendix discusses the factors influencing crack lengths as calculated using compliance measurements on WOL, i.e. $MC(W_b)$, specimens.

KEY WORDS

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

GENERAL COMMENTS OF REVIEWER

This is non-critical review.

RELATED HLW REPORTS

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

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

(a) Relationship to Waste Package Performance Issues Already Identified

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

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

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

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

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

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

TYPE OF DATA

(1) Scope of the Report

Experimental laboratory data

(2) Failure Mode or Phenomenon Studied

Fatigue crack growth

MATERIALS/COMPONENTS

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

TEST CONDITIONS

(1) State of Materials Tested

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

Two tables contain the A36 and A387-9 compositions and mechanical properties. For A36 (Pohang heat Y45659): composition (weight percent) C = 0.15, Si = 0.2, Mn = 0.96, P = 0.23, S = 0.014, Cu = 0.02; yield strength = 45.8 ksi, ultimate strength = 67.8 ksi, elongation = 28.0 percent, reduction in area not given. For A387-9 (Armco heat 45862): composition (weight percent) C = 0.11, Si = 0.23, Mn = 0.59, P = 0.012, S = 0.013, Mo = 0.94, Cr = 8.70; yield strength 75.8 ksi, ultimate strength = 99.5, elongation = 22.0 percent, reduction in area = 65.7 percent.

(2) Specimen Preparation

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

(3) Environment of the Materials being Tested

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

METHODS OF DATA COLLECTION/ANALYSIS

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

AMOUNT OF DATA

Five figures are given which plot the logarithm of the fatigue-crack-propagation (FCP) rate (da/dN) as a function of the logarithm of the stress-intensity factor range (∓K). The units of da/dN are inches/cycle and of ∓K are psi•$in^{1/2}$.

Figure 1 is titled "Fatigue-Crack Growth Behavior of Wrought A36 Steel Tested in an Air Environment at 150°C."
Figure 2 is titled "Fatigue-Crack Growth Behavior of Wrought A36 Steel Tested in an Air Environment at 250°C."
Figure 3 is titled "Fatigue-Crack Growth Behavior of Wrought A387 Grade 9 Steel Tested in an Air Environment at 150°C."
Figure 4 is titled "Fatigue-Crack Growth Behavior of Wrought A387 Grade 9 Steel Tested in an Air Environment at 250°C."
Figure 5 is titled "Fatigue-Crack Growth Behavior of Cast A27 Grade U-60-30 Steel Tested in an Air Environment at 150°C."

Individual regression lines for the various material/temperature combinations are plotted in Figure 6 titled "Comparison of the Fatigue-Crack Growth Behavior of Steels Tested in an Air Environment." Table 5, "Crack Growth Equation Constants," gives the constants in the crack growth equation for these experiments.

UNCERTAINTIES IN DATA

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

DEFICIENCIES/LIMITATIONS IN DATABASE

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

KEY WORDS

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

GENERAL COMMENTS OF REVIEWER

Non-critical review.

RELATED HLW REPORTS

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

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

(a) Relationship to Waste Package Performance Issues Already Identified

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

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Rockwell International, Rockwell Hanford Operations, Richland, Washington.

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

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

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

TYPE OF DATA

(1) Scope of the Report

Experimental determination of slow strain rate and fracture mechanics data.

(2) Failure Mode or Phenomenon Studied

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

MATERIALS/COMPONENTS

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

The above are candidate container materials.

TEST CONDITIONS

(1) State of the Material being Tested

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

(2) Specimen Preparation

For slow strain rate tests no information is given.

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

(3) Environment of the Material being Tested

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

METHODS OF DATA COLLECTION/ANALYSIS

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

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

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

AMOUNT OF DATA

There are seven tables.

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

There are ten figures. The first two are schematic diagrams of fracture mechanics data.

Figure 1--"Schematic Relationship Between Applied Stress, Crack Size, and Threshold Stress Intensity Factor."
Figure 2--"Threshold Stress Intensity Factor and Fracture Mechanics Data."

The next five figures are graphs containing slow strain rate data. Reduction of area in percent (0 to 70) is plotted against strain rate in reciprocal seconds (10^{-7} to 10^{-3}).

Figure 3--"Slow Strain Rate Results for 1020 Wrought Carbon Steel (150°C)."
Figure 4--"Slow Strain Rate results for A27 Case Carbon Steel (150°C)."
Figure 5--"Slow Strain Rate Results for A387 Low-Alloy Steel (150°C)."
Figure 6--"Slow Strain Rate Results for 90-10 Cupronickel (100 and 200°C)."
Figure 7--"Slow Strain Rate Results for Oxygen-Free High-Conductivity Copper (100 and 200°C)." In this graph the reduction in area ranges from 0 to 30 percent.

The last three figures (8, 9, and 10) contain fatigue crack growth data obtained in the cyclic tests. Fatigue crack growth rate, da/dN, in mm/cycle (10^{-6} to 10^{-3}) is plotted versus stress-intensity factor range, ΔK, in $MPa \bullet m^{1/2}$.

Figure 8--"Fatigue Crack Propagation in Carbon Steels at 250°C," shows data for A36 in air, vacuum and a groundwater, and for A27 in the groundwater at 250°C.
Figure 9--"Fatigue Crack Propagation in A36 Steel at 150°C," shows data in air, vacuum, and groundwater.
Figure 10--"Fatigue Crack Propagation in A387 Steel at 250°C,"
shows data in air and vacuum.

UNCERTAINTIES IN DATA

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

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Experimental data, linear-elastic fracture mechanics (LEFM), microscopy, visual examination, slow strain rate, laboratory, air, basalt composition, simulated groundwater, Cl, SO_4, H_3SiO_4, Na, basalt, bentonite, high temperature, high pressure, hydrostatic head, basic (alkaline) solution (pH >7), static (no flow), dynamic (flow rate given), copper base, carbon steel, low-alloy steel, 1020 carbon steel, A27, A387, OFHC Copper (UNS C10200), Cupronickel 90-10 (UNS C70600), annealed (Cupronickel), cast (A27), wrought (1020)

(OFHC Copper), tempered (A387), slow strain rate, bolt or wedge loading, prestressed (during exposure), crack elongation, corrosion (stress cracking) SCC, fatigue (corrosion), cracking (stress corrosion) SCC, cracking (environmentally assisted).

GENERAL COMMENTS

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

RELATED HLW REPORTS

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

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

(a) Relationship to Waste Package Performance Issues Already Identified

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

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Pacific Northwest Laboratory, Richland, WA 99325.

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

Westerman, R. E., Haberman, J. H., Pitman, S. G., Pulsipher, B. A., Sigalla, L. A., "FY 1984 Annual Report - Corrosion and Environmental-Mechanical Characterization of Iron-Base Nuclear Waste Package Structural Barrier Materials", PNL-5426, March 1986. Available from NTIS.

DATE REVIEWED: 7/29/87; Revised 9/30/87.

TYPE OF DATA

Experimental data.
Uniform corrosion, non-uniform corrosion (pitting), stress corrosion cracking (slow-strain-rate and corrosion-fatigue tests).
Statistical analyses.

MATERIALS/COMPONENTS

Waste package overpack
ASTM A216 grade WCA cast steel
- as cast (majority of tests)
- normalized (930°C/1 h/air cool)
- homogenized (930°C/24 h/air cool)

ASTM A27 grade 60-30 cast steel
- as cast
- normalized (927°C/5 h/air cool)

AISI 1025 wrought steel
- hot rolled

2.5Cr - 1Mo cast steel
- as cast

ASTM A536-77 ductile cast iron, grade 60-40-18
- as cast

High-purity iron (99.87% Fe)

Note: ASTM A216 test samples obtained from single 352 lb. casting with minimum dimension of 4.7 in. Casting/plate sizes for other materials not given.

TEST CONDITIONS

Three synthetic Permian Basin aqueous brine environments, PBB1, PBB2, and PBB3:

(1) intrusion brines (saturated brine) simulating (a) dissolution of salt horizon core (PBB1) and (b) supernatant fluid above precipitated solids after heating brine to 150°C (PBB2).

(2) high Mg inclusion brine (PBB3).

Tests conducted:

(1) Intrusion brine tests conducted in flowing autoclave tests at 150°C with PBB2 brine under both "anoxic" (~50 ppb O_2) and "oxic" (~1.5 ppm O_2) conditions.

(2) Intrusion brine tests in irradiated flowing autoclaves with PBB2 brine at 150°C. ^{60}Co gamma-radiation intensities of 1×10^5 and 2×10^3 rd/h. Specimens with artificial pits included.

(3) Moist salt exposures in sealed cans at 150°C. Dried PBB1 or reagent grade NaCl with liquid added as PBB1, PBB3 or saturated NaCl brine.

(4) Slow-strain-rate tests (SSR) in flowing PBB2 brine and in air at 150°C with strain rates of 2×10^{-7}/s and 1×10^{-4}/s. Inlet oxygen levels of 0.1, 1 and 2-3 ppm. Some tests run with pre-exposed specimens.

(5) Corrosion fatigue tests with notched compact tension specimens exposed in air, deionized water and PBB2 brine at 150°C. Tests conducted at frequencies of 0.1, 1 and 10 Hz.

METHODS OF DATA COLLECTION/ANALYSIS

Corrosion rates based on weight loss versus time. Measurements were taken after descaling with formaldehyde-inhibited HCl. Analysis of corrosion products by X-ray diffraction and chemical analysis. Reduction-in-area and elongation measurements of specimens in SSR tests, energy-absorption calculations, metallographs and scanning electron micrographs of fracture surfaces. Crack-growth rates recorded as function of stress intensity in corrosion fatigue tests.

AMOUNT OF DATA

Eleven tables in text plus 19 tables in Appendix. 33 figures.

Table 1 - Compositions of cast and wrought ferrous materials ASTM A216 Grade WCA, ASTM A27 Grade 60-30, AISI 1025 wrought steel, 2.5Cr-1Mo cast steel, ASTM A536-77 Grade 60-40-18, high purity iron. Weight percent of C, Mn, Si, P, S, Mo, Cr, Ni, Fe

Table 2 - compositions of synthetic brines (ion, concentration - mg/l)

	PBB1	PBB2	PBB3
Na^+	123,000	123,000	23,200
Ca^{2+}	1,560	1,110	14,700
Mg^{2+}	134	122	53,200
K^+	39	39	10,500
Sr^{2+}	35	35	--
Zn^{2+}	8	8	8
Cl^-	191,000	191,000	210,000
SO_4	3,200	1,910	160
HCO_3	30	23	--
Br^-	32	24	2,400
F^-	1	1	--

Table 3 - List of materials included in general corrosion/intrusion brine corrosion studies - anoxic and oxic test conditions, A216, A27 (as cast and normalized), 1025 steel, ductile iron, 2.5Cr - 1Mo cast steel, high purity iron. Exposure times of 7 to 21 months, 5 to 13 duplicate specimens tested under each condition.

Table 4 - Comparisons of estimated corrosion rates for general corrosion in anoxic simulated inclusion brine PBB2 at 150°C. Corrosion rates range from 4.8 to 14.6 μm/y with standard errors of 0.71 to 1.11.

Table 5 - Similar to Table 4, data for oxic brine. Corrosion rates range from 10.1 to 25.2 with standard error of 0.68 to 1.06.

Table 6 - Corrosion rates of reference A216 Grade WCA steel in moist salt environments - 150°C, 1 month, 20 percent H_2O. Corrosion rates range from 4.3 to 4.8 μm/y in NaCl/NaCl brine, 10 to 11 in PBB1/PBB1 brine and 580 to 910 μm/y in PBB1/PBB3 brine.

Table 7 - List of materials included in irradiation-corrosion studies.
A216, A27 (as cast and normalized), 1025 steel, ductile iron, 2.5Cr-1Mo steel, high-purity iron, ^{60}Co gamma radiation intensities of 1 x 10^5 and 2 x 10^3 rd/h with maximum exposure times of 5 to 18 months. Seven to fourteen reduplicate specimens included in each test.

Table 8 - Comparison of corrosion rates (8.4 to 48.4 μm/y) in 150°C, PBB2, 2 x 10^3 rd/h test vs exposure time (1300 to 9000 h) and top, center and bottom locations in autoclave.

Table 9 - Same as Table 8, 1 x 10^5 rd/h. Corrosion rates range from 37 to 185 μm/y.

Table 10 - Statistical analysis of results of slow-strain-rate tests. Standard errors for reduction of areas range from 26 to 70 in air and 15 to 72 in PBB2 brine. Ranges for elongation range from 18 to 31 percent in air and 13 to 32 percent in PBB2 brine.

Table 11 - Results of slow-strain-rate tests on A216 at 30°C and 90°C with strain rate of 2 x 10^{-7}/s and irradiation intensity of 3 x 10^5 rd/h.

Approximately 19 additional tables included in Appendices - tabulate detailed data for all tests:

Appendix A - general corrosion tests
Appendix B - moist salt studies
Appendix C - irradiation-corrosion studies
Appendix D - slow-strain-rate and corrosion-fatigue tests
Appendix E - compilation of statistical data

Figure 1 - Schematic of flowing autoclave test

Figure 2 - Schematic of moist salt test configuration

Figure 3 - Schematic of irradiation-corrosion test facility

Figure 4 - Schematic of slow-strain-rate test system (unirradiated)

Figure 5 - Schematic of slow-strain-rate test system (irradiated)

Figure 6 - Schematic of corrosion fatigue test facility

Figure 7 - Metal penetration rate vs. time with 95 percent confidence limits - A216 steel, 150°C, PBB2 brine, unirradiated. Penetration rates range from 10 to 40 $\mu m/y$ with exposures of up to 6000 hours.

Figure 8 - Corrosion rates of A216, 1025 steel and ductile cast iron in dried synthetic PBB1 salt/PBB3 brine as a function of water content. One month at 150°C. Corrosion rates range from 0.1 to 0.75 $\mu m/y$ for water contents of 18 to 32 percent.

Figure 9 - Same as Figure 8, 3 month exposure. Similar range of corrosion rates.

Figure 10 - Corrosion rate vs. Mg content of brine. Moist salt test with A216 cast steel. Corrosion rates range from 4 to 700 $\mu m/y$ with Mg contents ranging from 0 to 3 percent.

Figure 11 - As cast A216 specimen surface microstructure after moist salt test (PBB1/PBB3)

Figure 12 - Effect of 1×10^5 rd/h radiation on corrosion of ferrous materials in PBB2 intrusion brine at 150°C. Maximum corrosion rate is 200 $\mu m/y$, maximum exposure time is 21 months.

Figure 13 - Comparison of ferrous materials in intrusion brines irradiated at 1×10^5 and 2×10^3 rd/h. Units same as figure 12.

Figure 14 - Mean penetration rates for A216 in irradiated PBB2 brine at 150°C. Corrosion rates of 10 to 25 $\mu m/y$ for 2×10^3 rd/h and 100 to 150 $\mu m/y$ for 1×10^5 rd/h. Maximum exposure time is 6000 h.

Figure 15 - Photo of A27 specimen after PBB2 brine exposure with 1×10^5 rd/h. Illustrates spalling of corrosion product.

Figure 16 - Scanning electron micrograph of surface film on ASTM A27 specimen exposed 6 months in PBB2 with 2×10^3 rd/h.

Figure 17 - Schematic of pitting corrosion specimen (drilled holes to simulate pits)

Figure 18 - Photograph of corrosion sample with artificial pits - exposed 4 months in PBB2 with 1×10^5 rd/h.

Figure 19 - SSR data for 1025 steel in 150°C PBB2 brine and air - reduction in area (10 to 70 %) vs strain rate (10^{-7} to 10^{-4}).

Figure 20 - SSR data for A27 cast steel - similar to figure 19

Figure 21 - SSR data for A27 cast steel in PBB2 brine at 150°C - energy absorbed (2 to 8 kg-m) with strain rates of 10^{-7} to 10^{-4}.

Figure 22 - SSR data for A27 cast steel in 150°C PBB2 sparged with Ar, Ar-20% O_2 and O_2 - energy absorbed (3 to 5 kg-m) versus solution oxygen content (relative values).

Figure 23 - SSR data for A27 cast steel in 150°C PBB2 - effect of pre-exposure on energy absorbtion (1 to 8 kg-m) at 10^{-4} strain rate.

Figures 24-26 - Scanning electron micrographs of A27 cast steel SSR test specimen fracture surfaces - illustrate different fracture modes, pitting and cracking associated with porosity defects.

Figure 27 - SSR data for A216 cast steel in air at 150°C - reduction in area and elongation (10 to 40%) versus strain rate (10^{-7} to 10^{-4}).

Figure 28 - Similar to figure 27 - data for PBB2 brine.

Figure 29 - 1025 steel corrosion fatigue data for deionized water, air and PBB2 brine. Crack growth rate (10^{-8} to 10^{-4} m/cycle) vs stress intensity (20 to 60 MPa$\sqrt{m}$).

Figure 30 - Similar to figure 29 - data for A216 cast steel in air and deionized water.

Figure 31 - Similar to figure 29 - data for A216 is deionized water comparing frequencies of 0.1 and a Hz.

Figure 32 - Similar to figure 29 - data for A216 in PBB2 brine and air.

Figures 33a and 33b - Low magnification photographs of fatigue cracks in A216 specimens, before and after cleaning.

UNCERTAINTIES IN DATA

Author includes extensive statistical analysis of data reliability.

DEFICIENCIES/LIMITATIONS IN DATABASE

Author notes (1) controversy over use and existence of "threshold" stress intensity for corrosion failure predictions, (2) difficulties in extrapolation of short-term corrosion rates to significantly longer exposure periods, (3) complications due to corrosion product buildup in corrosion fatigue specimen notch, and (4) unexplained effects of sample location in irradiated autoclave tests.

KEY WORDS

Data analysis, experimental data, corrosion, microscopy, visual examination, weight change, simulated field, laboratory, brine, brine (high ionic content), brine (low ionic content), ^{60}Co, high temperature, static (no flow), dynamic (flow rate given), steel, carbon steel, 1025 carbon steel, A216 grade WCA, A27 grade 60-30, 2.5Cr-1Mo, A536 grade 60-40-18, high-purity iron, cast, homogenized, normalized, slow strain rate, modified compact, precracked, chloride, corrosion (general), corrosion (pitting), fatigue (corrosion), cracking (environmentally assisted).

GENERAL COMMENTS OF REVIEWER

This is a detailed review of broad-based corrosion studies to assess suitability of ferrous materials for use as waste package overpack. The program addresses general corrosion in simulated inclusion and intrusion brines, irradiation effects and environmental cracking based on slow-strain-rate and corrosion fatigue tests. The report acknowledges the potential importance of bacterial corrosion and hydrogen embrittlement in overall material degradation model but does not reference related data.

The report weakens arguments for use of corrosion fatigue studies to assess environmental cracking susceptibility. This is done by an acknowledgment of the controversy over the concept of a threshold stress intensity in a dynamic corrosion environment, and of the problems with corrosion-product buildup in the specimen notch. The buildup prevents crack closure during the low-stress portion of a fatigue cycle (this increases K_{min} and decreases ΔK).

The large majority of the tests on the reference cast steel (A216 grade WCA) were conducted with as-cast samples from a single casting.

Statistical comparisons of corrosion data from multiple castings should be considered. The report discounts potential mechanical or corrosion-related effects that could result from specific heat treatments. This is an area that needs better understanding to delineate overpack fabrication restrictions.

Perhaps the most significant observation is the corrosion acceleration effects in the simulated PPB3 inclusion brine. These effects are attributed to the higher Mg^{2+} content. The significance of these effects and the corrosion mechanisms involved need detailed study.

RELATED HLW REPORTS

Westerman, R. E., Haberman, J. H., Pitman, S. G., and Perrin, J. S., "Corrosion of Iron-Base Waste Package Container Materials in Salt Environments," Nuclear Power Conference, Philadelphia, PA, PNL-SA-14029, July 20, 1986.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues 2.2.4.1, what are the rates of corrosion as a function of time for the various corrosion modes of the waste package container, and 2.4, how and at what rates will radionucides migrate through failed waste package?

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

The disposal of high-level nuclear waste in deep underground repositories may require the development of waste packages that will keep the radioisotopes contained for time periods up to 1000 years. The primary geologic media currently being considered in the United States for repository siting are salt, basalt, tuff, and granite. A number of iron-base materials are being considered for the structural barrier members of waste packages. Their uniform and nonuniform (pitting and intergranular) corrosion behavior and their resistance to stress-corrosion cracking in aqueous environments relevant to salt media are under study at

Pacific Northwest Laboratory (PNL). The purpose of the work is to provide data for a materials degradation model that can ultimately be used to predict the effective lifetime of a waste package overpack in the actual repository environment. This report summarizes the results of the studies conducted at PNL during the FY 1983-FY 1984 time period in support of the Salt Repository Project of the Department of Energy.

The corrosion behavior of the candidate materials was investigated in simulated intrusion brine (essentially NaCl) in flowing autoclave tests at 150°C, and in combinations of intrusion/inclusion (high-Mg) brine environments in moist salt tests, also at 150°C. Studies utilizing a ^{60}Co irradiation facility were performed to determine the corrosion resistance of the candidate materials to products of brine radiolysis at dose rates of 2×10^3 and 1×10^5 rd/h and a temperature of 150°C. These irradiation-corrosion tests were "overtests," as the irradiation intensities employed were 10 to 1000 times as high as those expected at the surface of a thick-walled waste package.

Slow-strain-rate (SSR) tests and corrosion fatigue tests conducted in intrusion brine environments at 150°C and, in the case of some SSR tests, with a superimposed radiation field of 3×10^5 rd/h, were used to determine the resistance of the candidate alloys to environmentally enhanced crack propagation.

With the exception of the high general corrosion rates found in the tests using moist salt containing high-Mg brines, the ferrous materials exhibited a degree of corrosion resistance that indicates a potentially satisfactory application to waste package structural barrier members in a salt repository environment.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Pacific Northwest Laboratory, Richland, Washington 99352.

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

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

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

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-di) 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 was determined by SEM/EDX. The corrosion data was 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 Deionzed 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

Figures

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 Tr(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.

KEY WORDS

Data analysis, experimental data, literature review, theory, leaching, leachate analysis by ICP spectrometry, atomic absorption, calorimetry, laboratory, air, CO_2 free air, deionized, simulated groundwater, acid solution (pH <7), basic (alkaline) solution (pH >7), dynamic (flow rate given), high temperature, acidic solution buffered by CO_2, glass, SRL-TDS 131m PNL-76-68.

GENERAL 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."

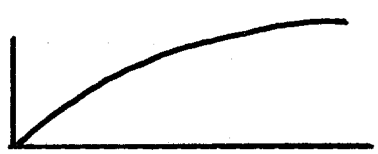
It must be concluded that the quantitative effects of glass composition on leaching have not been determined. It could be done with a great deal more work. The question is whether this effort will be useful in predicting long-term leach rates. Although nuclear waste glasses would be marginally durable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

<u>Leachant Flow Rate Effect</u>

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.

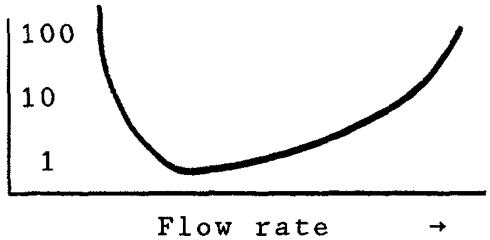
The effect of flow rate of the leachant on the leach rate is unequivocal, and this is recognized in the general glass-durability literature. It is obviously a result of the change in leachant composition as the glass reacts with the leachant.

In quantitive 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 quidelines 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 H_3O+ 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 Stabilty 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 Data

Pacific Northwest Laboratories, Richland, WA 99352.

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

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

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

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.
Na_2O, CaO, SrO, Cs_2O, Li_2O, Al_2O_3, DWRG glass, Fe_2O_3, UO_3, B_2O_3, Deionized water, Groundwater SiO_2, H_4SiO_4, $Mg(OH)_2$, 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: $10^{-14}10^{-12}$ mol/s.

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° 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: 0.1-10m^2/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 H_4SiO_4 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:$SiOz(OH)_2^{-2}$(aq) + $2H^+$(aq) = SiO_2(sol) + H_2O 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/mol 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/mol for pH range: 5-12.

7.13 Estimated stability of component Al_2O_3. Free energy of formation range: -1720-(-1600) kJ/mol 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/mol for S/V range: 0-2000.

7.15 Estimated stability of component silica versus S/V. Free energy of formation range: -920-(-800) kJ/mol 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/mol 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/mol 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/mol 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/mol 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/mol 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/mol 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/mol 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/mol 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/mol 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/mol 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/mol 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/mol and pH range: 9-10.5.

7.28 Estimated free energies of formation of oxide components of leached residues from DWRG glass. Deionized and groundwater leachant at 373°K. Free energy of formation range: -770-(-)650 kJ/mol and pH range: 9-11.5.

7.29 Estimated free energies of formation for silica in leached residues from DWRG glass. Deionized and groundwater leachant at 373°K. Free energy of formation range: -920-(-) 800 kJ/mol and pH range: 9-11.5.

7.30 Estimated free energies of formation for boron oxide in leached residues from DWRG glass. Deionized and groundwater leachant at 373°K. Free energy of formation range: -1200-(-)1320 kJ/mol and pH range: 9-11.5.

7.31 Estimated free energies of formation for alumina in leached residues from DWRG glass. Deionized and groundwater leachant at 373°K. Free energy of formation range: -1750-(-)1630 kJ/mol and pH range: 9-11.5.

7.32 Estimated free energies of formation for iron oxide in leached residues from DWRG. Deionized and groundwater leachant at 373°K. Free energy of formation range: -720-(-)600 kJ/mol and pH range: 9-11.5.

7.33 Estimated free energies of formation for uranium oxide in leached residues from DWRG glass. Deionized and groundwater leachant at 373°K. Free energy of formation range: -1180-(-)1060 kJ/mol 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 mol 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 mol 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.

KEY WORDS

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

GENERAL 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.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues 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, and 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.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

The Catholic University of America, Washington, D.C.

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

Barkatt, A., Macedo, P. B., Sousanpour, W., Boroomand, M. A., Szoke, P. and Rogers, V., "Aluminosilicate Saturation as a Solubility Control in Leaching of Nuclear Waste-Form Materials," PNL-4382, August 1982. Available from NTIS.

DATE REVIEWED: 9/16/87.

TYPE OF DATA

Experimental study of glass leaching.
Predictive model for solubility and leach rates.

MATERIALS/COMPONENTS

Five waste-form materials and various basalt, granite and kaolinite minerals.

TEST CONDITIONS

Glasses were in solid form for most tests; some static tests used crushed powders. Except for the powders, specimen preparation methods were not specified. Test environment was water at 70°C under slow-flow conditions.

METHODS OF DATA COLLECTION/ANALYSIS

Chemical analysis of leachants, method unspecified.

AMOUNT OF DATA

Four tables

1. Results of Dynamic Leach Tests on Various Waste Form Materials in the Slow Flow Region, 70°C. (Leachant concentration vs residence time for five waste form glasses.)

2. Silica and Alumina Content of Various Nuclear Waste Solids and Rock Specimens, Weight Percent.
3. Composition of Rock Leachants in Laboratory Test and Nature.
4. Al:Si Mole Ratios in Solid and Leachate Compositions.

One Figure

1. AlxSi and $(AlxSi)^2$ Concentration Products in Saturated Leachates of Nuclear Waste-Form Materials and of Rock Materials at 70°C and in Basaltic Groundwater as a Function of pH.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

Conclusions of the present paper require further experimental confirmation. Comprehensive analyses of leachants corresponding to very long contact times of waste forms with water and of aged groundwater from geologic formations are needed. The influence of low-solubility species on leachate saturation levels should be studied further.

KEY WORDS

Experimental data, laboratory, PH, flow rate, significant dissolve species concentration, Al-Si, sorption, leaching.

GENERAL COMMENTS OF REVIEWER

The fact that the solubility of silica in aqueous media is lower when alumina is present in the system has been reported in the literature, and lower solubility of alumina in the presence of silica has likewise been reported. [In this paper the authors specify the concentration product (C_{Al} x C_{Si}) by using either the symbols AlxSi or the symbol/term Al-Si concentration product.]

The primary objective of the paper is to demonstrate that the solubilities of various waste glasses and minerals are controlled by the product of the concentrations of aluminum and silicon in the leachate. The authors hypothesize that the solubilities of aluminum and silicon are controlled by readsorption of a combined (and equimolar) aluminosilicate (Al-Si) species. At a slow-flow rate characteristic of geologic repositories, this product is governed by temperature and pH of the leachate. Thus, accurate predictions of long-term leach rate can be made for a repository providing the limits are known for pH and temperature. However, in slow flow conditions, which commonly lead to saturation for all of the main glass constituents, the minor glass constituents leach much more slowly. This decreased rate of leaching is due to the presence of the re-adsorbed Al and Si, which block the exposure (to the leachate) of the minor constituents.

The need for additional data, as stated by the authors, is well taken.

RELATED HLW REPORTS

Barkatt, Aa., Barkatt, A., Pehrsson, P. E., Szoke, P., and Macedo, P. B., "Static and Dynamic Tests for the Chemical Durability of Nuclear Waste Glass," Nucl. Chem. Waste Management, Vol. 2, pp. 151-164, 1981.

APPLICABILITY OF DATA TO LICENCING
[Ranking: key data ( ), supporting data (X)]

(a) Relationship to Waste Package Performance Issues Already Identified

Related to issues 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 forms under the range of repository conditions, 2.3.2.1, what are the possible dissolution mechanism of the waste form under the range of potential repository conditions, 2.3.2.1.1, which waste form dissolution mechanism or mechanisms are most likely, and 2.3.2.1.1, what are the rates of dissolution associated with the potential form dissolution mechanism?

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

In the slow flow region, material loss rates of nuclear waste form materials are determined by the solubilities and the flow rates. Present studies show that the solubilities of various, widely different waste forms, as well as of minerals, can be correlated with the AlxSi concentration products. This indicates that in these cases the solubilities are controlled by a combined equimolar aluminosilicate species. This observation serves as a basis for a predictive model for the long-term stability of waste forms under slow flow conditions. This model also provides explanations of other experimental findings, such

as the increases in solubility upon departure from a neutral pH in the low as well as in the high PH region, the small magnitude of the temperature dependence, and the observation that the release rate of Cs is low relative to that of Na in the slow flow region. The relative concentrations of Si and of Al, respectively, in the leachates are related to the composition of the leach solids and are shown to depend on the immersion time in different ways in the cases of high-silica solids and of high-alumina solids, respectively. In both cases, however, the dependence of the Si:Al ratio on contact time furnishes another strong indication for the formation of a solid surface with comparable contents of Al and of Si, respectively, upon prolonged immersion in water. The results are shown to form the basis for an accurate long-term prediction of material loss rates.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Catholic University of America, Washington, DC.

(a) Author(s), Reference, Reference Availability

Feng, X. and Barkatt, Aa., "Solubility Tests on Borosilicate Glasses for West Valley Waste Immobilization, High-Level and Transuranic Waste Management," Trans. Am. Nucl. Soc., 53, 133-135, 1986.

DATE REVIEWED: 4/28/87; Revised 10/13/87.

TYPE OF DATA

Experimental results of systematic leaching tests on West Valley glasses.

MATERIALS/COMPONENTS

West Valley Glass, SRL Glass.

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

MCC-3 static leach test.

AMOUNT OF DATA

2 Tables:

1. Solubility Tests - MCC-3.
2. IAEA Tests on Glass A at pH 10.4 ± 0.1.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITTATIONS IN DATABASE

None given.

KEY WORDS

Experimental data, sampling, weight change, laboratory, air, buffered media, basic (alkaline) solution (ph >7), dynamic (flow rate given), defense high level waste (DHLW), buffered water, leaching (radiation enchancement).

GENERAL COMMENTS OF REVIEWER

MCC-3 leach tests on West Valley related glasses indicate that the ionic strength of the leachants have a significant effect on the leach rates of the glass and that the leach rates are insensitive to substitution of K^+ for Na^+ in the leachant.

This is an extended abstract, with two detailed tables, summarizing results of leach tests on West Valley related glasses. The authors conclude from these tests that the ionic strength of the leachants may have a significant effect on the leach rates. This tentative conclusion needs further investigation.

A critical review of this work will be given after a full report on this work is published.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), Supporting (X)]

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issue 2.3.2, what is the solubility of the waste form under the range of potential repository conditions?

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

West Valley Nuclear Services Company, Inc., West Valley, NY.

(a) Author(s), Reference, Reference Availability

Barnes, S. M., Chapman, C. C., Petkus, L. L., Murawski, T. F., and Pope, J. M., "Startup and Initial Experimental Results for the West Valley Vitrification Demonstration Project," Waste Management' 86 Proceedings, Tucson, Arizona, March 2-4, 1986, pp. 441-448.

DATE REVIEWED: 4/27/86, Revised 10/13/87.

TYPE OF DATA

Experimental results summarizing the testing completed to date. Plans are presented for the remaining cold testing at West Valley.

MATERIALS/COMPONENTS

Concentrator, ADS pumps, Melter, Turntable, Bed Scrubber, high-efficiency mist eliminator (HEME), high-efficiency particulate air (HEPA), Off-Gas Equipment, LIEF, process canister (PORCAN), Canister.

TEST CONDITIONS

Full-scale test of process equipment with cold materials.

METHODS OF DATA COLLECTION/ANALYSIS

Experimental tests.

AMOUNT OF DATA

Tables

1. Vitrification Equipment Installation and Initial Testing Dates.

2. WVDP Vitrification Test Summary, Including Dates, Run Description, Feed Type, Glass Feed Composition, Volume of Slurry Fed, Concentration of Oxides in Feed and Amount of Glass Collected.

Figures

1. West Valley High-Level Waste Processing Schematic Flowsheet.

2. Off-Gas and Vessel Vent System. Block Diagram.

3. West Valley Full Scale, Integrated Process Testing Plan.

4. Generic FACTS Run Logic.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Experimental data, technological experimental data, sampling, visual examination, field, defense high-level waste (DHLW).

GENERAL COMMENTS OF REVIEWER

This is an updated general paper about the West Valley vitrification demonstration project. The paper includes general descriptions of some of the processes and detailed information on the concentrator, ADS pump, melter, turntable, and bed scrubber. Also provided are descriptions of the High Efficiency Mist Eliminator (HEME), High-Efficiency Particulate Air (HEPA) filter assembly, and the off-gas equipment composed of packed and bubble cap NO_x scrubbing columns arranged in series.

The paper includes initial experimental results from preliminary tests of the process. The first experiments are described, including the canister deformation test under filling process, slurry-fed equipment test, test of concentrator as a feed tank, test of ADS pump, and the processing of the hydroxide based, simulated WV-205 waste slurry. The suction canister technique was tested to demonstrate the capability of removing the glass from the melter in the event that the melter must be shut down if required. The off-gas equipment was tested when nitrated slurry feed was processed.

Initial data for the process/product correlation (which will be used to calculate the glass composition from the concentrator sampling) was collected after installation of the C-sampler in the concentrator.

To date, a total of 41,500 liters of simulated waste slurry was fed to the melter and 28,400 Kg of glass was collected, during 17 process runs.

Future plans for full-scale testing between the date of issuing the paper and hot operation are laid out.

Cooling the turntable by external water will rapidly cool the glass and may cause cracks in the glass block. It is very important to measure these cracks because the leach rate may depend on the glass surface area, e.g. at high water flow rates.

It is not clear how the problem of feed segregation in the concentrator will be solved (see experiment SF-5). It is not obvious how addition of "appropriate amounts of B, K, Li and Na" to the slurry can change this segregation (experiment SF-6) without changing the composition of the glass in the last canister. We believe that an important issue in this work is the degree of homogenization of the sludge in the melter, at it relates to homogeneity within a canister and from one canister to another.

One of the important parameters that could help our understanding of the homogenization process is the Residence Time Distribution (RTD) in the melter. This parameter depends on the viscosity, temperature, density, and feed rate. It is possible to measure the RTD as a function of the process parameters using a radioactive tracer technique.

These measurements together with other measurements discussed in this report, and, most importantly, occasional sampling of the glass form would appear to be acceptable. It is our understanding that WVDP has now agreed to undertaking spot sampling of the glass waste form.

<u>RELATED HLW REPORTS</u>

1. Wolf, D. and White, D. H., "Experimental Study of The Residence Time Distribution in Plasticating Screw Extruder" AICHE Journal, <u>22</u>, 122-131, 1976.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), Supporting (X)]

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issue 2.3.1, what are the physical, chemical and mechanical properties of the waste form?

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

JRC, Ispra, Varese, Italy, and GNSM and University of Moderna, Moderna, Italy.

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

Manara, A., Antonini, M., Camagni, P., and Gibson, P. N., "Radiation Damage in Silica-Based Glasses: Point Defects, Microstructural Changes and Possible Implications on Etching and Leaching," Nuclear Instruments and Methods in Physics Research, B1, 475-80, 1984.

DATE REVIEWED: 3/17/87, Revised 10/9/87.

TYPE OF DATA

Experimental and data analysis. Radiation damage to surfaces of silica and borosilicate glasses.

MATERIALS/COMPONENTS

Silica and borosilicate glasses.

TEST CONDITIONS

Materials subjected to bombardment by H^+, He^{+2}, Ne^{+3}, Ni^{+6}, and e^-. Some specimens were subjected to double irradiation using two of the bombardment ions.

METHODS OF DATA COLLECTION/ANALYSIS

Irradiated materials were etched using dilute HF. Correlations were made between bleaching of color centers and thermal annealing. Effects of irradiation on the glasses were determined using controlled etching and step-height observations. Volume expansion of the irradiated layer was estimated by counting and measuring the sizes of bubbles formed. Penetration depth as calculated by computer code EDEP-1 was compared with coloration depth. Depths of etching were measured with a Talystep-1 instrument.

AMOUNT OF DATA

Eleven Figures

1. Saturation values of various intrinsic color center bands in irradiated SiO_2 as a function of impinging particle mass; optical density at saturation (scale not defined) vs mass of impinging ion for e^-, H^+, He^{+2}, Ne^{+3}, and Ni^{+6} (0 to 60 amu).
2. Effects of double irradiation on vitreous SiO_2 after Ni-ion irradiation and after further proton irradiation. Optical density (0.0 to 0.5) vs energy in ev (3 to 7).
3. Effects of double irradiation on vitreous SiO_2, after Ni irradiation and after further alpha irradiation. Optical density (0.0 to 0.50 vs energy (3 to 9 ev).
4. Residual coloration of Ni-irradiated vitreous silica after progressive etching of damaged surface. Five curves showing optical density (scale not defined) vs wavelength(nm) before etching and after etching of 2.8, 5.8, 8.8, and 10.8 microns.
5. Penetration profiles of the 46.5 Mev nickel ion in vitreous SiO_2 (computer code EDEP-1). Dose in direct atomic displacements (dpa), (0 to 1.5) vs depth (0 to 10 microns).
6. Effect of various irradiations on the etching/time characteristics of vitreous SiO_2. Etched depth (0 to 14 microns) vs etching time (0 to 6 minutes) for unirradiated, 1 Mev protons, (0.1 dpa) and 20.5 Mev neon ions (0.1 dpa).
7. Isochronal annealing curves for the excess etching rate (0 to 4 micrometer/min) and normalized optical density (0 to 1) vs temperature (0 to 700°C).
8. Isochronal annealing of the excess etching rate in Ne^{+3} irradiated and unirradiated vitreous SiO_2, etching rate (0 to 4 micrometer/min) vs annealing temperature (0 to 900°C).
9. Bubble density and total swelling vs dose in electron irradiated borosilicate glass; left scale, total swelling (0 to 50%), right scale, bubble density (0 to 10 bubbles/m^3).
10. Total swelling rate as a function of irradiation temperature in borosilicate glasses of varying sodium content. Swelling rate (0 to 15 illegible units) vs irradiation temperature (200 to 700 K) for 19, 25, and 4% Na_2O borosilicate glasses.
11. Micrograph of the electron-irradiated region of a borosilicate glass.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

The authors have not performed systematic measurements of the doses necessary to initiate an increase in the etching rate. There is a lack of information on the dose dependence and saturation behavior.

KEY WORDS

Data analysis, experimental data, supporting data, radiation damage, surface etching, volume expansion, EDEP-1, laboratory, glass, borosilicate glass, silica glass.

GENERAL COMMENTS OF REVIEWER

Radiation damage on the microstructural level of host borosilicate glasses may impact on leaching behavior. Bubble formation leads to a decrease in the glass density in the damaged layer. Experimental evidence indicates bubble formation is associated with breaking Na-O bonds in the glass which leads to high O_2 concentration in the bubbles and aggregations of colloidal Na elsewhere. Although there is evidence in the literature that radiation damage to the glass does not increase the leach rate significantly, other data suggests that after a critical dose of radiation, a large increase in leach rate of up to a factor of 50 could occur. However, measurements of leach-rate data were not made in these experiments. Measurable structural damage is expected to begin after a cumulative dose of 10^{23} alpha decays per m^3 and would be expected to occur within the first 10,000 y in a geologic repository. This issue appears to warrant additional consideration.

RELATED HLW REPORTS

1. Burns, W. G. and Hughes, A. E., Marples, J. A., Nelson, R. S., and Stoneham, M. A., "Effects of Radiation Damage on the Leaching of Vitrified Waste, "Scientific Basis for Nuclear Waste Management V, W. Lutze (editor), Elsevier Science Publishing Co, Amsterdam, The Netherlands, p 339, 1982.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to issue 2.3.2.1 concerning the possible dissolution mechanisms of the waste form under the range of potential repository conditions.

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

The Pennsylvania State University, University Park, PA 16802.

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

Komarneni, S., Freeborn, W. P., Scheetz, B. E., and McCarthy, G. J., "Reaction and Devitrification of a Prototype Nuclear Waste Storage Glass with Hot Magnesium-Rich Brine," ONWI-305, October 1982. Available from NTIS.

DATE REVIEWED: 10/26/87; Revised 11/30/87.

TYPE OF DATA

Experimental results from leaching tests of PNL 76-68 prototype waste glass that was reacted with NBT-6a(Ca-Mg-K-Na-Cl) brine at 100, 200 and 300°C.

MATERIALS/COMPONENTS

PNL 76-68 Prototype waste glass, NBT-6a brine.

TEST CONDITIONS

The experiments described in this report were carried out at 100, 200 and 300°C and 30 MPa total pressure.

METHODS OF DATA COLLECTION/ANALYSIS

High-pressure leaching tests (not a standard test); visual examination by binocular microscope at up to 40X magnification; X-ray diffraction for crystalline identification; qualitative elemental analysis for elements heavier than neon obtained by Energy Dispersive X-ray Spectrometry(EDX) on a Scanning Electron Microscope(SEM); compositional profiles of reacted and recrystallized glass shards obtained with the Electron Microprobe. All the elements except Cs, Rb, Zn and U were analyzed with computer-interfaced Atomic Emission Spectrometer(AES). The elements Cs, Rb, and Zn were analyzed by Atomic Absorption Spectrophotometry(AAS). Uranium was determined by a fluorometric method.

AMOUNT OF DATA

13 Tables and 22 Figures

Tables

1. Composition of PNL 76-68 Glass.
2. Composition of NBT-6a Brine.
3. Hydrothermal Reaction Experiments with Borosilicate Glass and Brine.
4. Comparison of Selected X-ray Powder Data from the 21-Day 300°C Treatment (GB-131) with Talc Data in the Powder Diffraction File.
5. Gandolfi X-ray Patterns for Black Spheres Taken from Run GB-131.
6. Solution Concentration (12.5:1 NBT-6a brine to glass treated at 100°C/30 MPa).
7. Solution Concentration (12.5:1 NBT-6a brine to glass treated at 200°C/30 MPa).
8. Solution Concentration (12.5:1 NBT-6a brine to glass treated at 300°C/30 MPa).
9. Average Solution Concentration and Percent of Element in Solution (12.5:1 NBT-6a brine to glass treated at 100°C/30 MPa).
10. Average Solution Concentration and Percent of Element in Solution (12.5:1 NBT-6a brine to glass treated at 200°C/30 MPa).
11. Average Solution Concentration and Percent of Element in Solution (12.5:1 NBT-6a brine to glass treated at 300°C/30 MPa).
12. Least Squares Fitting Parameters for Temperature Dependence of Brine-Extracted Elements.
13. Percentage of Initial Inventory Detected in Solution Brine Extraction from PNL 76-68. (4 weeks; 30 MPa; Glass:Solution = 1:12.5 brine, 1:10 water)

Figures

1. Photomicrographs of fragments of PNL 76-68 glass after hydrothermal reaction with NBT-6a brine. Upper figure, Run GB 128 (300°C; 14 days); lower figure Run GB 4 (300°C; 28 days).
2. Mat of fine-grained talc coating the inside of the gold tube. Run GB 133, 1000X.
3. Euhedral crystal of powellite, $CaMoO_4$. The grid of small crystals is recrystallized gold. Run GB 137, 200X.
4. Small spherical grains of specular hematite with euhedral gold on a talc background. Run GB 133, 200X.
5. Closeup of individual sphere. 1000X.

6. Spherical grain of uranium-rich unknown phase on background of talc. Run GB 131. 2500X.
7. Energy spectrum of uranium-rich unknown phase.
8. X-ray diffractograms of PNL 76-68 glass after treatment in NBT-6a brine for the time indicated (7-56 days).
9. Polished section of glass after hydrothermal reaction presented as SEM mosaic. Run GB-4 (300°C, 300 bars, 28 days). Arrows show direction of electron microprobe traverse. Sequence of short parallel white streaks are caused by the electron beam.
10. Microprobe traces of glass reacted at 200°C for 4 weeks.
11. Microprobe analyses of glass reacted at 300°C for 1 week.
12. Microprobe traces of glass reacted at 300°C for 2 weeks.
13. Microprobe analyses for glass reacted at 300°C for 3 weeks.
14. Microprobe analyses of glass reacted at 300°C for 4 weeks.
15. Microprobe analyses of additional elements in 300°C, 2 week reaction.
16. Schematic drawing of main reaction layers in PNL 76-68 glass reacted hydrothermally with Ca-Mg brine.
17. Thickness of reaction rind as function of reaction time.
18. Time dependence of the percentages of elements extracted into solution.
19. Time dependence of the percentages of elements extracted into solution.
20. Average concentrations of extracted elements as a function of run temperature. Open circles are the concentrations of the same elements in deionized water at 300°C and 30 MPa.
21. The concentration of silica, expressed as elemental Si, in solution at various run times. Data for deionized water are from McCarty, G. J., et al., "Hydrothermal Stability of Simulated Radioactive Waste Glass," ACS Advances in Chemistry Series No. 168, 349-389, 1980.
22. Average solubility of silica, expressed as SiO_2, in deionized water and brine compared with the solubility of crystalline quartz and amorphous silica. Solid circles are average SiO_2 concentrations in brine runs at each temperature; open circle is average SiO_2 concentration in deionized water from McCarty, G. J., et al., "Hydrothermal Stability of Simulated Radioactive Waste Glass," ACS Advances in Chemistry Series No. 168, 349-389, 1980.

UNCERTAINTIES IN DATA

All specimens that were tested contained opaque regions formed by crystalline inclusions. It should be noted that the ratio of these crystalline phases to glass was not constant from specimen to specimen. Because of the variability of the amounts of these inclusions, it is estimated that the actual composition of an element in a particular specimen could vary by as much as 10-20 percent of the nominal composition.

In table IV, sample X-ray data are compared to data for talc found in the X-ray powder diffraction file. Although the resemblance is not sufficient to allow an unambiguous identification of talc by bulk X-ray characterization alone, a comparison with Gandolfi data on the white mat-like linings of the capsules leaves little doubt as to the identification.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Experimental data, microscopy, laboratory, air, brine (high ionic content), salt, high pressure, high temperature, static (no flow), PNL-76-68, devitrification (glass) maxtrix dissolution (glass).

GENERAL COMMENTS OF REVIEWER

Leaching tests of PNL 76-68 nuclear-waste glass were carried out under hydrothermal conditions at 100, 200, and 300°C with NBT-6a (Ca-Mg-K-Na-Cl) brine (Magnesium-rich brine). Microscopic, electron microprobe, SEM observation and analytical results were used to identify the reaction products. Depending on time and temperature, glass fragments were leached to depths of 300-500 μm. The concentration of silica in brine solution was lower by an order of magnitude when compared with the concentration of silica in deionized water reacted under similar conditions.

The most prominent feature of the chemical concentration profiles established by the microprobe is the sodium-potassium exchange front. The activity of sodium is higher in the glass with the result that sodium diffuses out of the glass and potassium diffuses in. The alkali metal ions are more mobile than other ions and the Na-K exchange front penetrates most deeply into the glass. A sharp increase in sodium concentration and abrupt decrease in the potassium concentration occur at various depths in the glass, depending on temperature and reaction time and are called the "Na-K front". This front moved 130 μm into the glass in 1 week at 300°C, and after 2 weeks advanced 400 μm. However, longer reaction times did not produce greater penetration. According to one hypothesis, this steady-state thickness represents the lag between the faster diffusion processes and the slower dissolution with the breakdown and removal of the glass-forming network.

The quantities of glass enclosed in the experimental capsules varied from run to run, but in all cases the brine was added as a 12.5:1 weight ratio.

It is our understanding, that the more important parameter in such kinetic experiments is the surface-to-volume ratio. This is the reason that the results are qualitative; they do not take into account surface-to-volume (S/V) effects. The small shards of glass used in these experiments have much higher S/V ratio than would massive ingots of the same materials.

It was found that the total quantity of the alkaline metals strontium and barium extracted is about two orders of magnitude higher in brine than in deionized water. Also, the alkali metals cesium and rubidium are about a factor 10 more concentrated in the brine solution than in deionized water. These results are very important for leaching processes in nuclear-waste glass in which the main radionuclides are strontium and cesium; therefore, it is very important to develop a theory to explain these results.

Aspects of this study were not performed in accordance with approved procedure, and the data cannot be used for licensing purposes.

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, what is the solibility of the waste form under the range of potential repository conditions?

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

PNL 76-68, a prototype nuclear waste storage glass, was reacted under hydrothermal conditions at 100, 200, and 300°C with NBT-6a (Ca-Mg-K-Na-Cl) brine. Reaction products were identified, the state of the residual glass determined, and the concentrations of various elements remaining in the solutions analyzed. Solid products formed by reaction of the glass and brine were talc (hydrated magnesium silicate), powellite ($CaMoO_4$), hematite (Fe_2O_3) and rarely an unidentified uranium-containing phase. Glass fragments were leached to depths of 300 - 500 μm, depending on time and temperature. Most elements were extracted, but the silicate framework remained intact. Distinct diffusion fronts due to K/Na exchange and Mg/Zn exchange were identified. A complex compositional layering develops in the outer reaction rind. The concentration of silica in brine solution was lower by an order of magnitude than the concentration of silica in deionized water reacted under similar conditions. The concentration of cesium, strontium, uranium, rare earths, and other alkali and alkaline earth elements in solution increases exponentially with temperature of reaction. Behavior of the transition metals is more complex. In general the extraction of elements from the glass by hydrothermal brine leads to concentrations in solution that are from 10 to 100 times higher than the concentrations obtained by deionized water extraction under similar conditions of temperature and pressure.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Savannah River Plant, Aiken, SC.

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

"Savannah River Interim Waste Management Plan - FY-1987," DOE/SR-WM-87-1, September 1986. Available from NTIS.

DATE REVIEWED: 5/22/87; Revised 10/13/87; 11/20/87.

TYPE OF DATA

Program plan. The plan was developed to provide a working knowledge of the nature and extent of the interim waste management programs being undertaken by Savannah River contractors for Fiscal Year 1987. In addition, the document projects activities for several years beyond 1987 in order to adequately plan for safe handling and storage of radioactive wastes generated at Savannah River, and for developing technology for improved management of low-level solid wastes. Work descriptions and milestone schedules are current as of the date of publication.

MATERIALS/COMPONENTS

Waste storage tanks, waste storage sites, tank farm evaporator, cesium removal columns.

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

None given.

AMOUNT OF DATA

25 tables and 50 figures

This report provides a excellent summary of the updated Savannah River waste management program.

Tables

Figures

E - 1 : Long Range Salt Removal.

E - 2 : Waste Removal and Extended Sludge Processing Schedule.

G.1-1 : Groundwater Surveillance Wells. Area Map.

G.1-2 : F-Area Tank Farm Groundwater Monitoring Wells.

G.1-3 : H-Area Tank Farm Groundwater Monitoring Wells.

G.1-4 : F- and H-Area Seepage Basin Groundwater Monitoring Wells.

G.1-5 : F- and H-Area Tank Farm Dry Monitor Wells.

G.2-1 : Burial Ground Wells.

G.2-2 : Solid Waste Storage Facility Well Locations.

G.2-3 : Burial Ground Showing Zones of Trench Alpha, Intermediate and Low-Level Beta-Gamma Waste, and Solvent Storage.

A.I-1 : Waste Evaporator. Principal Features.

A.III-1: Type I Waste Storage Tanks.

A.III-2: Type II Waste Storage Tanks.

A.III-3: Type III Waste Storage Tanks.

A.III-4: Removable Cooling Coil, Type III Tanks.

A.III-5: Insertable Coolers for Type III Tanks 29-35.

A.III-6: Type IIIA Waste Storage Tanks.

A.III-7: Type IV Waste Storage Tanks

UNCERTAINTIES IN DATA

A test conducted in 1983 showed that zeolite could not be removed from the tanks by agitation alone, as is done for sludge removal. This is not yet understood and work is continuing on developing a practical method for sludge removal.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Design, experimental data, planned work, field, Savannah River Plant, stainless steel, steel, carbon steel, defense high level waste (DHLW), groundwater, corrosion (general), corrosion (pitting), corrosion (stress cracking) SCC, fracture (brittle), cracking (stress corrosion) SCC.

GENERAL COMMENTS OF REVIEWER

This NBS review contains only a summary of the contents of the technical report. It contains neither critical commentary nor analyses by NBS staff and it will be included in the "Database for Reviews and Evaluations on High-Level Waste (HLW) Data."

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), Supporting (X)]

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issue 2.3.2.1, what are the physical, chemical and mechanical properties of the waste form?

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

This document provides the program plan as requested by the Savannah River Operations office of the Department of Energy. The plan was developed to provide a working knowledge of the nature and extent of the interim waste management programs being undertaken by Savannah River (SR) contractors for the Fiscal Year 1987. In addition, the document projects activities for several years beyond 1987 to adequately plan for safe handling and storage of radioactive wastes generated at Savannah River and for developing technology for improved management of low-level solid wastes.

A revised plan will be issued prior to the beginning of the first quarter of each fiscal year. In this document, work descriptions and milestone schedules are current as of the date of publication. Budgets are based on available information as of June 1986.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

The Catholic University of America, Washington, D. C.

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

Barkatt, Aa., Adiga, R., Adel-Hadadi, M., Barkatt, Al., Freeborn, W., Macedo, P., Montrose, C., Mohr, R., Mowad, R., and Sousanpour, W., "Chemical Durability Studies on Glass Compositions Pertaining to Waste Immobilization at West Valley," Waste Isolation in the U.S. Technical Programs and Public Education, March 1986.

DATE REVIEWED: 4/30/87; Revised 12/3/87.

TYPE OF DATA

Experimental data on glass leaching.

MATERIALS/COMPONENTS

Four borosilicate glass compositions were studied:

1. West Valley Reference Glass (WVRG)
2. Defense Waste Reference Glass (DWRG)
3. Experimental Glass A: low alumina, melted at West Valley
4. Experimental Glass B: higher silica, lower boron than WVRG, melted at Catholic U.

TEST CONDITIONS

Three types of leach tests were used:

1. Frequent exchange, modified IAEA/ISO test
2. Partial exchange pulsed flow test
3. MCC-1 static test

All tests were carried out with deionized water at 90°C.

Glass specimens:

Leach tests 1 and 3 used rectangular glass blocks, 200 grit cut surface, surface area = 400 mm^2. Pulsed-flow test samples were -40/+60 mesh powdered glass. In the pulsed-flow test, the leachant volume was 100 mL. A volume of 25 mL was periodically withdrawn and replaced with 25 mL of fresh deionized water.

METHODS OF DATA COLLECTION/ANALYSIS

Leachate analysis: methods not specified, but were previously cited in references 3, 5, and 10 of the paper. Reference 10 states that leached species were determined by a.c. plasma spectrometry. Exceptions were Li and Cs, which were determined by flame emission, and Mg, which was determined by atomic absorption.

AMOUNT OF DATA

Four Tables

1. Composition of Tested Glasses.
2. Results of Modified IAEA Test (Leaching rates of eight elements from glass A and DWRG).
3. Results of MCC-1 Leach Test (Leaching rates of 14 elements from DWRG and two samples of WVRG).
4. Results of Pulsed Flow Leach Test (Leaching rates of 14 elements from WVRG, DWRG, glass A, and glass B).

UNCERTAINTIES IN DATA

Uncertainties are listed for leach rates.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Basic solution, deionized DWRG glass, experimental data, glass, high temperature, laboratory, leach, WVRG glass.

GENERAL COMMENTS OF REVIEWER

The purpose of the work was to characterize the chemical durability of the currently proposed West Valley Reference Glass (WVRG) under long term, as well as short term, leach conditions and to investigate the behavior of two other glasses having acceptable melting ranges for processing. The report presents leach data for four glasses using three types of leach tests. The data do substantiate that, under the test conditions used, West Valley Reference Glass (WVRG) and Defense Waste Reference Glass (DWRG) are similar in behavior and are both considerably more durable than glasses A and B, which are designed to be processible. The modified IAEA/ISO test indicated that the dissolution was nearly congruent except for highly insoluble components such as Fe and Mn. The MCC-1 tests showed no significant differences between the WVRG-I, WVRG-II, and Defense Waste

Reference Glass (DWRG) during the corrosion process which was nearly congruent. Pulse-flow tests, carried out with powdered glass samples and high S/V ratios, indicated saturation effects for all four glasses. These effects resulted in suppression of leach rates of all glass components. The normalized elemental release rate of the WVRG glass is about 20 percent greater than the DWRG glass.

It is stated that the suppression of the leach rates is due to formation of alteration products. No evidence for this is provided in this report. The authors attempt to rationalize some of the leach results in terms of the composition of the glasses. They suggest that key factors affecting leach rates are the pH, which is a function of alkali and B_2O_3 content, and the amount of Al_2O_3, which decreases the leach rate. However, these arguments are not very convincing because the authors tend to select one or two composition differences on an ad hoc basis to explain the difference in leach rates.

The authors also address the suitability of the test methods used. In the modified IAEA/ISO test and the MCC-1 test, saturation behavior was not approached. In the pulsed flow test, the contact time is longer and saturation rather than matrix corrosion is claimed to be the controlling factor. Individual and relative corrosion rates of various glasses may vary significantly depending on the controlling mechanism. As a result, the implication, of both the present work and other work by the same group, is that the pulsed-flow test is superior for predicting long-term leaching behavior.

<u>RELATED HLW REPORTS</u>

Barkatt, Aa., Macedo, P. B., Sousanpour, W., Barkatt, Al., Boroomand, M. A., Fisher, C. F., Shirron, J. J., Szoke, P., and Rogers, V. L., Nuclear and Chemical Waste Management, <u>4</u>, 153-169, 1983.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues, 2.3, when, how, and at what rate will radionuclides be released from the waste form, 2.3.2.11, which waste form dissolution mechamism or mechanisms are most likely, 2.3.2.1.2, and what are the rates of dissolution associated with the potential waste form dissolution mechanisms?

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

Leach tests have been initiated on several borosilicate glass compositions produced upon vitrification of simulated West Valley high-level wastes. The current reference composition exhibits low leach rates, similar to those of the current reference defense waste glass composition, in tests providing for both short and long contact times of the glass with water. Tests on experimental glasses which have significantly different compositions from that of the reference glass (in particular, a low B_2O_3 or Al_2O_3 content) indicate that such changes in composition can cause considerable increases in leach rates, especially at long contact times.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Materials and Components Technology Division, Argonne National Laboratory, Argonne, IL 60439.

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

Chopra, O. K. and Chung, H.M., "Aging Degradation of Cast Stainless Steel," Presented at 14th Water Reactor Safety Information Meeting, October 1986.

DATE REVIEWED: 5/21/87; Revised 8/24/87.

TYPE OF DATA

Experimental data relating to mechanisms for embrittlement of cast austenitic/ferritic stainless steels thermally aged a 350-450°C.

MATERIALS/COMPONENTS

CF-3, CF-8, CF-8M cast stainless steels (equivalent to wrought stainless steels 304, 316 and 317). Nineteen experimental heats (static cast keel blocks), six commercial heats (centrifugally cast pipe and static cast pump components), one BWR recirculating pump cover plate. Ferrite contents of individual heats range from 4 to 28 percent.

TEST CONDITIONS

Examination of thermally aged cast stainless steel, aging times up to 70,000 hours (8 years). BWR pump cover plate with twelve years service also examined.

METHODS OF DATA COLLECTION/ANALYSIS

Mechanical tests and microstructural studies to define embrittlement mechanisms:

- charpy impact
- tensile tests
- J-R tests (fracture toughness)
- scanning electron microscopy (SEM)
- transmission electron microscopy (TEM)
- small angle neutron scattering (SANS)
- atom probe field ion microscopy (APFIM)
- extraction replicas

AMOUNT OF DATA

Ten micrographs with phase identifications and fracture surfaces. Tabular and graphical presentation of Charpy V-notch impact, J, J_{IC} and tensile data as function of thermal aging. Maximum aging temperature reported is 450°C.

Two Tables summarizing Charpy V-notch impact data and tensile properties as a function of aging times for cast duplex stainless steels. Charpy values range from 8 to 401 J/cm^2 for ferrite contents of 4 to 28 percent, yield stresses from 213 to 300 MPa at room temperature and 153 to 180 MPa at 288°C, axial and circumferential ultimate stresses range from 548 to 677 MPa at room temperature and 396 to 502 MPa at 288°C, axial and circumferential reduction in area ranges from 56 to 80 percent at room temperature and 56 to 85 percent at 288°C.

Figure 1 - Schaffler diagram - ferrite content of cast duplex stainless steels as function of Ni and Cr equivalents
Figures 4 & 5 - atomic percent Cr, Ni and Fe profiles in ferrite phase of GF heat 280 specimen aged at 300°C for 70000 hours and BWR pump cover after 12 years service
Figures 6, 7 & 8 - Charpy V-notch impact energy (20 to 500 J/cm^2) as function of aging parameters for CF-3, CF-8 and CF-8M cast stainless steels
Figure 11 - Charpy V-notch load-time curves for single heats of CF-3 and CF-8 cast stainless steels. Maximum load is 25 kN, maximum time is 2 ms.
Figures 12 & 13 - Influence of test temperature on Charpy V-notch impact energy for aged and unaged CF-3 (two commercial heats) and CF-8 BWR reactor cover plate.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

Data does not clarify interactions between spinodal decomposition and gamma phase precipitation changes with aging temperature. Understanding of interaction is considered important to help define kinetic effects on embrittlement.

KEY WORDS

Data analysis, experimental data, literature review, theory, sampling, neutron diffraction, x-ray diffraction, spectroscopy, tensile testing, impact test, laboratory, ambient temperature, liquid nitrogen, stainless steel, cast stainless steel, CF-3, CF-8, CF-8M cast stainless steel, cast, elongation/reduction in area, tensile strength, yield strength, charpy impact properties, J-R curve, J_{Ic}, thermal embrittlement.

GENERAL COMMENTS OF REVIEWER

This is a comprehensive review of thermal embrittlement of cast austenitic/ferritic duplex stainless steels with emphasis on light-water reactor components. It clearly identifies the need for better understanding of decomposition and related embrittlement processes, particularly with regard to interactions between the Cr-rich α' phase and the Ni- and Si-rich G-phase within the range of in service aging temperatures. Similar embrittlement phenomena are of importance in nuclear waste containment vessels utilizing cast alloy components. In comparison with wrought alloys of similar composition, which are normally fully austenitic, controlled ferrite contents are specified in cast alloys to assure adequate castability and weldability. The data included in this report help quantify the sluggish kinetics of the decomposition reactions at repository temperatures and the need for long-term exposures. The report refers to planned exposures of up to 50,000 h. Results should help clarify results presented in this report.

RELATED HLW REPORTS

Chopra, O. K. and Chung, H. M., "Aging of Cast Duplex Stainless Steels in LWR Systems," Nuclear Engineering and Design, 89, 305-318, 1987, North-Holland, Amsterdam, Elsevier Science Publishers.

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

(a) Relationship to Waste Package Performance Issues Already Identified

This work is related to ISTP issue 2.2.3, regarding possible failure modes of the waste package container.

(b) New Licensing Issues

(c) General Comments on Licensing

Appendix B. Database Keyword Checklist Tree and Keyword Checklist

MAJOR & SUBCATEGORIES OF THE KEYWORD CHECKLIST TREE

A. TECHNICAL DESCRIPTION OF REPORT

1. Scope of Work
2. Applicability of data to licensing
3. Model/methodology
4. Names of computer programs discussed
5. Measurement methods

B. ENVIRONMENTAL FACTORS OF THE TESTS

6. Testing site
7. Geographic location of field site
8. Gaseous environment
9. Aqueous environment
10. Ionic or other chemical species present
11. Solid material environment
12. Radiation environment
13. Experimental/test conditions

C. MATERIALS TESTED (Metallic, Non-metallic, Radioactive, Environmental)

a. Metallic Waste Package Components Tested

14. General material type
15. Specific material designation
16. Condition prior to test
17. Test specimen specification

b. Non-metallic Waste Package Components Tested

18. Non-metallic waste form

c. Radioactive Waste (Radionuclides and Fuel) Materials Tested

19. Radioactive waste form
20. Radionuclides

d. Environmental Materials Tested

21. Kind of water present
22. Electrolytes present
23. Environment solids

D. PROPERTIES AND FAILURE MODES STUDIED

24. Physical properties studied
25. Failure mode

KEYWORD CHECKLIST

A. TECHNICAL DESCRIPTION OF REPORT

1. Scope of Work
    __data analysis
    __design
    __experimental data
    __literature review
    __planned work
    __theory
    __|other ______________________________

2. Applicability of data to licensing
    __key data
    __supporting data

3. Model/methodology
    __Latin hypercube
    __Monte Carlo
    __PDF (probability distribution functions)
    __general corrosion
    __leaching
    __pitting
    __sampling
    __scoping test
    __solubility
    __|other ______________________________

4. Names of computer programs discussed
    __MAKSIM
    __RADIOL
    __WAPPA
    __PROTOCOL
    __|other ______________________________

5. Measurement methods
    __adsorption
    __bent-beam test
    __corrosion
    __electrochemical
    __irradiation-corrosion test
    __linear-elastic fracture mechanics (LEFM)
    __microscopy (light, electron, SEM, etc.)
    __neutron diffraction
    __Rutherford Back Scattering (RBS)
    __slow-strain-rate test (SSR)
    __sorption
    __spectroscopy
    __surface film
    __tensile testing
    __visual examination
    __weight change
    __x-ray diffraction
    __|other ______________________________

Keyword Checklist

B. ENVIRONMENTAL FACTORS OF THE TESTS

6. Testing site
   __field
   __laboratory
   __simulated field

7. Geographic location of field site
   __Deaf Smith County
   __Hanford Reservation
   __Yucca Mountain
   __|other ______________________

8. Gaseous environment
   __air
   __carbon dioxide
   __|other ______________________

9. Aqueous environment
   __J-13 water
   __aerated water
   __basalt composition
   __brine
   __brine (high ionic content)
   __brine (low ionic composition)
   __deionized
   __distilled water
   __distilled-deaerated water
   __granite composition
   __groundwater
   __simulated groundwater
   __tuff composition
   __|other ______________________

10. Ionic or other chemical species present
   __Cl
   __Cu
   __Fe
   __Keller's reagent
   __Ni
   __S
   __|other ______________________

11. Solid material environment
   __basalt
   __bentonite
   __granite
   __salt
   __tuff
   __|other ______________________

12. Radiation environment
   __alpha radiation field
   __cobalt 60
   __gamma radiation field
   __|other ______________________

Keyword Checklist

13. Experimental/test conditions
- __acidic solution (pH <7)
- __ambient pressure
- __ambient temperature
- __basic (alkaline) solution (pH >7)
- __dynamic (flow rate given)
- __high pressure
- __high temperature
- __hydrostatic head
- __lithostatic pressure
- __neutral solution (pH = 7)
- __redox condition
- __static (no flow)
- __|other ______________________________

MATERIALS TESTED (metallic, non-metallic, radioactive, environmental)

a. Metallic Waste Package Components Tested

14. General material type
- __brass
- __bronze
- __carbon steel
- __cast iron
- __cast iron (gray)
- __cast iron (nodular)
- __cladding
- __copper base
- __nickel base
- __packing
- __stainless steel
- __steel
- __titanium base
- __weld
- __zircaloy
- __zirconium base
- __|other ______________________________

15. Specific material designation
- __1020 carbon steel
- __1025 carbon steel
- __304 stainless steel
- __304L stainless steel
- __308L stainless steel
- __308L weld filler wire
- __316ELC stainless steel
- __316L stainless steel
- __316NG stainless steel
- __317L stainless steel
- __321 stainless steel
- __347 stainless steel
- __CF-3 stainless steel
- __XM-19 stainless steel
- __zircaloy-2
- __zircaloy-4
- __|other ______________________________

16. Condition prior to test
- __annealed
- __annealed (mill)
- __annealed (austenitized and transformed)
- __case hardened
- __cast
- __cold worked
- __irradiated
- __magnetized
- __sensitized
- __sintered
- __solution treated
- __spent-fuel-rod with holes
- __spent-fuel-rod with slits
- __spent-fuel-rod with splits
- __spent-fuel-rod without defects
- __stress relieved
- __textured
- __welded
- __wrought
- __|other ______________________

17. Test specimen specification
- __bolt or wedge loading
- __modified compact (0.3< h/w <0.6)
- __precracked
- __prestressed (before exposure)
- __prestressed (during exposure)
- __slow strain rate
- __specimen thickness (inches) = 1T
- __specimen thickness (inches) = 2T
- __specimen thickness (inches) = 3T
- __specimen thickness (inches) = 1/2T
- __specimen thickness (inches) = 1/4T
- __specimen thickness (inches) = 3/4T
- __specimen thickness (inches) = 3/8T
- __standard compact (h/w = 0.6)
- __standard tensile (round type)
- __standard tensile (strip or strap type)
- __tensile loading
- __|other ______________________

b. Non-metallic Waste Package Components Tested

18. Non-metallic waste form
- __bentonite
- __glass (West Valley reference glass)
- __glass (defense waste reference glass)
- __|other ______________________

c. Radioactive Waste (Radionuclides and Fuel) Materials Tested

19. Radioactive waste form
    __commercial high-level waste (CHLW)
    __defense high-level waste (DHLW)
    __spent fuel
    __spent fuel (BWR)
    __spent fuel (LWR)
    __spent fuel (PWR)
    __uranium
    __|other ______________________

20. Radionuclides
    __Am241
    __Cm244
    __Co60
    __Cs137
    __I129
    __Np234
    __Np237
    __Np239
    __Pu237
    __Pu239
    __Pu240
    __Tc99
    __|other ______________________

d. Environmental Materials Tested

21. Kind of water present
    __J-13 steam
    __J-13 water
    __groundwater
    __|other ______________________

22. Electrolytes present
    __acetic
    __chloride
    __chloride (low ionic content)
    __chloride (high ionic content)
    __|other ______________________

23. Environment solids
    __basalt
    __bentonite
    __granite
    __salt
    __tuff
    __|other ______________________

Keyword Checklist

D. PROPERTIES AND FAILURE MODES STUDIED

24. Physical properties studied
__creep strength
__density
__elongation
__heat capacity
__modulus of elasticity
__stress or strain
__tensile strength
__thermal conductivity
__thermal expansion
__yield strength
__other ______________________________

25. Failure mode
__buckling
__corrosion (local)
__corrosion (crevice)
__corrosion (general)
__corrosion (pitting)
__corrosion (galvanic)
__corrosion (microbial)
__corrosion (irradiation)
__corrosion (intergranular)
__corrosion (stray current)
__corrosion (stress cracking) SCC
__cracking
__cracking (stress corrosion) SCC
__cracking (environmentally assisted)
__creep
__creep buckling
__dealloying
__debonding
__deformation (elastic)
__deformation (plastic)
__degradation (spent fuel)
__devitrification (glass)
__diagenetic-like changes
__dissolution
__fatigue (corrosion)
__fatigue (high cycle)
__fatigue (low cycle)
__fatigue (thermal)
__fracture (brittle)
__fretting
__hydration (glass)
__hydrogen attack
__hydrogen embrittlement
__leaching (spent fuel)
__leaching (radiation enhancement)
__matrix dissolution (glass)
__passivity
__poisoning (chemical)
__radiation effects
__rupture (ductile)
__rupture (stress)
__sensitization
__spalling
__thermal instability
__other ______________________________

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SEE INSTRUCTIONS ON THE REVERSE

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12 SUPPLEMENTARY NOTES

13. ABSTRACT (200 words or less)
This report summarizes evaluations made in the period August 1987 to January 1988 by the National Bureau of Standards (NBS) of Department of Energy (DOE) activities on waste packages for containment of high-level nuclear waste (HLW). The waste package will be part of a proposed engineered barrier system (EBS) in the permanent repository for HLW. Metal alloys are principal barriers within the EBS. The Budget Reconciliation Act for Fiscal Year 1988 provided that only the Yucca Mountain, NV, site (in which tuff is the geologic medium) shall be characterized for use as a HLW repository. Five reviews were completed for tuff covering ferrous alloys, copper, groundwater chemistry, and glass. Two issues were identified for the Yucca Mountain site: (1) the approach used to calculate corrosion rates for ferrous alloys, and (2) the observation of crevice corrosion in a copper-nickel alloy. It is noted that plutonium can form pseudo-colloids that may facilitate transport. NBS work related to the vitrification of HLW borosilicate glass at the West Valley Demonstration Project (WVDP) and the Defense Waste Processing Facility (DWPF) and activities of the DOE Material Characterization Center (MCC) is also included. Appended are NBS reviews of twenty other DOE technical reports and selected other reviews which, although conducted under the basalt and salt programs, are considered relevant to the present work on the tuff program. For these former candidate sites, technical discussions are given for the corrosion of metals proposed for the canister, particularly carbon steels, stainless steels, and copper.

14. DOCUMENT ANALYSIS - a. KEYWORDS/DESCRIPTORS

General Corrosion	Austenitic Stainless Steel	Nuclear Waste
Localized Corrosion	Copper	Tuff
	Borosilicate Glass	Salt
		Basalt

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