
Evaluation and Compilation of DOE Waste Package Test Data

Biannual Report: February 1988 – July 1988

Prepared by C. Interrante, E. Escalante, A. Fraker, E. Plante

U.S. Department of Commerce
National Institute of Standards and Technology

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Prepared by
C. Interrante, E. Escalante, A. Fraker, E. Plante

U.S. Department of Commerce
National Institute of Standards and Technology
Institute for Materials Science and Engineering
Metallurgy Division
Gaithersburg, MD 20899

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ABSTRACT

This report summarizes evaluations by the National Institute of Standards and Technology (NIST) of Department of Energy (DOE) activities on waste packages designed for containment of radioactive high-level nuclear waste (HLW) for the six month period February 1988 through July 1988. Activities for the DOE Materials Characterization Center are reviewed for the period January 1988 through June 1988. A summary is given of the Yucca Mountain, Nevada disposal site activities. Short discussions are given relating to the publications reviewed and complete reviews and evaluations are included.

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EXECUTIVE SUMMARY

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

The environmental conditions at the Yucca Mountain site and their pertinence in relations to technical issues are reviewed in this report. Six candidate materials are being considered for use in canisters. These materials are AISI 304L stainless steel, 316L stainless steel, high-nickel austenitic alloy 825, oxygen-free copper, Copper Development Association (CDA) 102, copper-7% aluminum bronze CDA 613 and 70-30 copper-nickel CDA 715. In this report, a NIST review discusses each of these materials.

Each of these candidate materials has specific problems and this is evident in both the published reports and the reviews. General concerns regarding these materials are (1) uncertainties, over time, associated with metastable materials such as the stainless steels, (2) phase stability and phase embrittling effects in the 825 alloy and (3) behavior of copper in oxic atmospheres, at temperatures of 270°C to 100°C, and in the presence of nitrogen compounds, and (4) the effects of gamma radiation on long-term performance.

Eighteen reviews of technical reports are included in this report. Six broad topics on materials are covered in these reviews: 1) the effect of irradiation on the pitting susceptibility of 316L, 2) the effect of long-term irradiation on the phase stability of austenitic stainless steels, 3) the susceptibility of 304L stainless steel to stress corrosion cracking (SCC) in water vapor, 4) the fractional release rates of the radionuclides and the effect of cladding deterioration on this rate, 5) the effect of localized condensation of nitric acid on the canister, and 6) the effect of copper ions on the pitting

susceptibility of Zircaloy. Other topics covered in the reviews include glass leaching, the processing of glass nuclear waste, and the environment. These topics are discussed in various reviews included here.

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1.0 INTRODUCTION

1.1 Background

This is the fifth biannual progress report to the Nuclear Regulatory Commission (NRC) from the National Institute for Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). These reports deal with the NIST assessments of the Department of Energy (DOE) activities related to the waste package for disposal of radioactive high-level waste (HLW).

The Nevada Nuclear Waste Storage Investigations (NNWSI) deals with the storage site at Yucca Mountain, Nevada. This site was selected in December 1987 as the primary site in the United States for the first nuclear waste repository. Each of the five NIST reports contains a section on the NNWSI and that section deals with NNWSI's waste package activities during a six-month period. This report covers the period from February 1988 through July 1988.

Approval of the Budget Reconciliation Act for Fiscal Year 1988 (Public Law 100-203) resulted in major changes in 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 site at Yucca Mountain, NV, as the proposed site for the first repository. Site-specific activities for the sites located at Hanford, WA, and Deaf Smith County, TX 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.

NIST activities under FIN A4171 henceforth will cover only NNWSI reports or other material pertinent to disposal of high-level waste at Yucca Mountain.

1.2 Reviews and Evaluations

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

In addition to considering ferrous alloys and the 825 nickel-base alloy, for use as container materials, copper and copper alloys are also being evaluated for the tuff repository site. In all, six candidate materials are discussed in Section 2.4 and in a review discussed on page 6. Eight other reports relating to canister materials and the environment are being considered by DOE and these materials are discussed both in Sections 2.4 through 2.5.2. The reviews are found on pages B-5 through B-96 of Appendix B.

The DOE is actively engaged in programs for the vitrification of high-level radioactive waste in borosilicate glass. Both the West Valley Demonstration Project (WVDP) at West Valley, NY, and the Defense Waste Processing Facility (DWPF) located at the Savannah River Plant in Savannah, GA, will soon be producing vitrified high-level waste (HLW). NIST activities in this area continue with five published reports and two chapters of PNL-5157 being reviewed during this reporting period. These reports are discussed in Section 3.0.1 and the reviews are found in Appendix B, pages B-56 through B-90.

The NNWSI Draft Site Characterization Plan (SCP) was reviewed at NIST and by others during this reporting period. NIST comments on the portions of the SCP dealing with the waste package are given in Appendix C.

Activities of the DOE-sponsored Materials Characterization Center (MCC) and the status of selected MCC test methods are briefly discussed in Section 4.0. Details are presented in Appendix D. The MCC monthly reports over the past two years show considerable progress on test development work for glass leaching.

1.3 Database Activities

Database activities focused on converting the NIST/NRC Database for Reviews and Evaluations on High-Level Waste to a new database management system (DBMS), Advanced Revelation®, and this has been completed. This DBMS has menu capabilities regarded to be superior to those developed at NIST for use with Revelation®. Conversion of the NIST/NRC files from the present DBMS, Revelation®, into Advanced Revelation® has been completed. 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.

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.

1.4 Related Laboratory Testing

Studies involving laboratory testing at the NIST 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 was released to the NRC in March 1988. The results of studies 2 and 3 are to be presented at the symposium on Corrosion of Nuclear Waste Containers at the 174th Meeting of the Electrochemical Society, October 9-14, 1988. Results from the other laboratory testing will be also published upon completion of selected parts of these works.

2.0 DOE Activities

Yucca Mountain was selected as the primary site in the United States for the first Nuclear Waste Storage area. The DOE has overall jurisdiction over the development of the Yucca Mountain site and works through the NNWSI and various national laboratories such as Lawrence Livermore (LLNL). The LLNL addresses the areas of design, testing and analysis of the waste package performance in the tuff environment.

The technical concerns of interest in this report are those pertaining to the waste package. They stem principally from the regulatory requirements for retrievability, containment and release, as given in 10 CFR Part 60 and 40 CFR Part 191. NRC regulation 10CFR60 requires substantially complete containment of radionuclides for between 300 to 1000 y. The regulation also requires that the nuclear waste must be retrievable for a period of 50 y, and requires that no more than one part in 10^5 of the inventory of radionuclides expected to be present at 1000 y after closure may be released annually. The environmental context in which these concerns are studied is that of the Yucca Mountain site.

2.1 Yucca Mountain -- Location and Environment

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

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

The repository will be located above the water table, and moisture will be present. At the present time, water flow is limited, and has been estimated to be six to eight millimeters per year, but this could change. The waste packages will be above the boiling point of water for many years and water vapor will be present. When the cooling period begins, small amounts of water will be present due to condensation and infiltration. Other sources of water

would be ground water from various sources and water which could be formed as a result of other reactions. Conditions of wetting and drying will exist, and the concentration of salts will be a result of this wetting and drying process.

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

2.2 Waste Package Materials

The DOE is conducting studies on selection of materials for the waste packages. The containers are a key part of the engineered barrier system. Under current study [McCright et al. 1987, see the NIST review in Appendix B, p. 23] are six candidate materials. Three are high alloy austenitic materials: AISI 304L and 316L stainless steels and the high nickel Alloy 825. The other three are in the copper family: Copper Development Association (CDA) 102, an oxygen-free pure copper; CDA 713, a 7% copper/aluminum bronze; and CDA 715, a 70-30 copper/nickel alloy.

Each of these candidate materials has specific problems, as is evident in the published reports and the reviews. In addition to the effects of gamma radiation, there are several concerns regarding these materials:

- a. Uncertainties over time associated with metastable materials, such as stainless steels.
- b. Phase stability and phase embrittling effects in Alloy 825.
- c. Behavior of copper in oxic atmospheres at temperatures of 270 to 100°C and in the presence of nitrogen compounds.

The following are some of the issues related to licensing:

- a. Effect of irradiation on the pitting susceptibility of 316L.
- b. The combined effects of long-term irradiation and elevated temperatures on the phase stability of austenitic stainless steels.
- c. Susceptibility of 304L to stress corrosion cracking (SCC) on long-term exposure to water vapor.
- d. Effect of localized condensation of radiolytically generated substances such as nitric acid on the waste containers
- e. Effect of copper ions on the pitting susceptibility of Zircaloy
- f. Effect of cladding deterioration on the fractional release rate of radionuclides.

Through review and evaluation of DOE documents, the NIST is providing technical expertise to the NRC for the assessment of DOE waste package designs and of DOE's ability to comply with regulatory requirements.

2.3 Vitrification activities

The DOE has active programs related to 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 (DPWF) at Savannah, GA will soon be in "hot" operations. Several issues stand out:

- a. The resistance of borosilicate glass to leaching by environmental water.
- b. The ability of the vitrification process to produce uniform product.
- c. The effects of radiolysis on the waste forms and on the waste package environment.

Current expectations are that most of the high-level waste initially placed in the repository will be spent fuel. Nevertheless, the imminence of hot operations at West Valley and Savannah River confers an urgency on the need to follow technical developments in the glass area. The NIST is providing technical expertise in this area partly through in-house staff and partly through outside consultants.

3.0 NIST Activities

3.1 Database Development

Conversion of the NIST/NRC Database for Reviews and Evaluations on High-Level Waste from the original database management system (DBMS), Revelation®, to a new DBMS, Advanced Revelation®, was completed. The new system has improved features, such as menus and popup screens, both of which permit multiple choices in the retrieval of data. It also informs the user about either the operation that is being conducted or the available choices for the next operation.

The keyword checklist and the keyword checklist tree were modified to incorporate a new field which contains a separate set of keywords for non-metallic waste forms.

Reviews are created using guidelines that describe the types of information to be contained in each section of a review. The current version of the guidelines is in Appendix A.

3.2 Reviews and Summaries

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

3.2.1 Candidate Canister Materials

The nuclear waste container will be exposed to constant irradiation by its highly radioactive contents, and it is imperative that a clear understanding of the effects of gamma radiation on the metal container be developed. The first study [Glass et al. 1986, see Appendix B, p. 18] in a series of seven reports evaluates the effects of gamma radiation on AISI type 316L stainless steel in J-13 water at 30°C. The results indicate that irradiation increases the oxidation potential of the aqueous environment through the production of OH⁻ and H⁺. The open-circuit potential of 316L becomes more positive (noble) in the presence of irradiation, probably due to these oxidizing species. The authors make the important conclusion that irradiation does not increase pitting susceptibility of 316L. This very important issue of the effect of radiation on pitting susceptibility will require an in-depth study.

Another report reviews the literature on phase stability and its effect on corrosion susceptibility of austenitic stainless steels [Bullen et al. 1987, see Appendix B, p. 5]. The review in this report, documents the metastable

nature of the austenitic phase in 304L and 316L. However, carbide precipitation, and the potential for sensitization, was found in all austenitic alloys considered, including the high-nickel 825 alloy. The data indicate that sensitization occurs very slowly at temperatures below 650°C, but in view of the extremely long containment time (300 to 10,000 y) required for service in the repository, these alloys might sensitize sufficiently to permit premature failure by stress corrosion cracking. An important issue not mentioned in this report is the effect of irradiation on phase stability.

The third report reviewed in this section deals with a study of the stress corrosion susceptibility of 304 and 304L stainless steels at elevated temperatures in the presence of irradiation and aerated water vapor [Westerman et al. 1987, see Appendix B, p. 38]. The results indicate that 304L, in its most corrosion resistant condition (solution annealed), failed by transgranular SCC in water vapor. This result is significant because it reveals stress corrosion susceptibility of a candidate alloy in simulated repository conditions. This is an important issue that requires further study.

The last report in this section [McCright et al. 1987, see Appendix B, p. 23] provides a very good description of the results of a compilation and review of testing barrier materials for the radioactive waste container as performed by the Lawrence Livermore National Laboratory and its subcontractors. This report lists six candidate waste canister materials and discusses associated problems as indicated in Section 2.4 of this report.

The authors state that austenite 304L and 316L stainless steels are metastable and subject to transformation to martensite, ferrite, sigma or other phases, thereby producing an increased tendency toward mechanical failure. The final closure welded joint could be a limiting point, and this question should be resolved. The authors indicate that concentration of ionic species could cause a problem with localized corrosion. Accelerated tests on 304L and 316L stainless steels in gamma radiation and an aqueous environment resulted in transgranular stress corrosion cracking (TGSCC), and this needs further study. Corrosion data on stainless steel obtained in an environment at a temperature near room temperature (28°C) over a period of one year, and other corrosion data, were used to extrapolate corrosion rates and to determine that a canister made of this material will not perforate in 1000 y [McCright et al. 1987]. More corrosion data are needed to support this analysis and to study effects of spalling, changing environment, and other factors.

3.2.2 Zircaloy Cladding

In boiling water reactors (BWR), plant corrosion products (crud) deposit on the fuel rods. Crud with high copper concentrations tends to form as a scale instead of as the usual fluffy iron-oxide crud. Crud-induced localized corrosion (CILC) of Zircaloy has been associated with the presence of copper, and copper has also been observed to accelerate zirconium alloy corrosion in acid environments. These observations, prompted a study to investigate the effect of copper on the corrosion of Zircaloy in a simulated repository environment [Smith 1987, see Appendix B, p. 91]. Under the simulated repository conditions, attack on zirconium alloys observed under other conditions (52°C and 1500 psi) could not be duplicated over a five-month period of exposure. The potential for localized corrosion in Zircaloy-clad fuel rods does exist, and these experiments should be repeated for a longer time at radiation levels simulating those in the tuff repository and with test conditions more conducive to CILC. The possibility of nodular corrosion and (CILC) of Zircaloy requires further study.

3.2.3 Waste Form

The vitrified waste studies include reviews of Chapters 2 and 5 from PNL-5157, which cover (1) surface layers in leached borosilicate glasses and (2) radiolysis effects on the waste form and local environment of the waste package. Four reviews relevant to waste handling at the Savannah River Plant (SRP) are included. These reports are overviews of strategies for (1) permanent storage of transuranic waste currently stored on the SRP site, (2) reduction of the volume of radioactive waste by removal of non-radioactive salt and sludge components for permanent storage as low level waste, (3) an overview of the planned vitrification process. A review of the strategy planned by the West Valley Demonstration Project (WVDP) to show compliance with high-level waste specifications is also included. The modeling paper involves tuff related modifications to a geochemical code (EQ3/6) for glass dissolution.

The other two reviews are on spent fuel and Zircaloy. Approximately 90 percent of all U.S. nuclear wastes are expected to be spent fuel. Thus, the integrity and durability of Zircaloy cladding and the various oxidation states (and their solubilities) of the spent fuel may be important in the release of radionuclides from the waste package. These two reviews deal with (1) crud-induced local failure corrosion of Zircaloy clad of BWR fuels and (2) radionuclide release from degraded LWR cladding.

3.2.3.1 Spent Fuel

The rate of dissolution of spent fuel is affected by the condition of the fuel. As the fuel oxidizes, its solubility in repository water increases. Further, the swelling of the fuel associated with oxidation can lead to splitting of the fuel-rod cladding; this exposes the spent fuel to further dissolution. A study by Wilson considers the effect of cladding degradation on the rate of radionuclide dissolution using LWR spent fuel, but no data are yet available [Wilson et al. 1985, see Appendix B, p. 95]. Previous studies using spent fuels taken from pressurized water reactors (PWR) indicate that (1) actinides are released congruently, (2) ^{137}Cs and ^{99}Tc are released preferentially when compared with release of the actinides, and (3) the fractional release rate of actinides was greater for the fuel without cladding when compared with that from the fuel with defective cladding. Due to both the importance of this issue on dissolution of spent fuel and the fact that spent fuel will be the major component of the buried waste (approximately ninety percent), more attention must be focused on understanding spent fuel dissolution and the factors that affect it.

3.2.3.2 Vitrified Waste

As part of a continuing effort to review the contents of PNL-5157, "Final Report of the Defense High Level Waste Leaching Mechanisms Program," reviews are given here for Chapters 2 and 5. Reviews of Chapters 1 and 7 have already been published in Volume 4 of NUREG/CR-4735. Chapters 3 and 6 are to be reviewed in Volume 6. Current plans include the review of Chapter 4 in Volume 7, and that will complete the set and invite the preparation of a summary of the contents of these seven reviews.

Chapter 2, "Surface Layers in Leached Borosilicate Glass High-Level Defense Nuclear Waste Forms [Mendel 1984; see Appendix B, p. 76] is an extensive review of data on alteration layers formed on the surface of leached borosilicate glass high-level defense nuclear waste forms. The leaching process apparently begins with replacement of the more soluble cations (boron, lithium, sodium) with ions from the leachant. Nonuniformities, such as cracks and surface roughness, accelerate the process by as much as an order of magnitude. Pit formation on the altered surface is common.

The interface between the altered glass and the bulk glass is physically and chemically well defined except for a reaction zone, generally less than 1 micron thick, which exhibits extensive pitting and depletion of the more soluble elements. The properties of the altered layer are

influenced by the reactions with the aqueous environment and are not due to diffusion effects. Dilute leachants produce thick low-density surface layers, whereas concentrated leachants produce thin high-density layers.

Reactive solids, such as canister metal or ductile iron, plus saturated deionized water result in significant acceleration of the removal of silica from the glass. This leads to the formation of colloidal complexes and well defined crystalline precipitates on the surface of the glass. In deoxygenated water, less reaction is observed.

This is an excellent review pertinent to understanding the altered layer but it does not discuss the implications of how the alteration layer is related to the problem of long-term leach modeling. Currently, some believe that the altered layer will act as a barrier and decrease the leach rate but others argue that the formation of crystalline deposits on the altered layer surface will increase the leach rate because the removal of silica from the leachate will increase the concentration gradient between the glass and the saturated leachate solution.

The review of Chapter 5, "Radiation Effects" [Mendel 1984; see Appendix B, p. 86], includes information pertaining to radiolysis effects relevant to salt or basalt repository sites and is not germane to radiolysis in a tuff site. Chapter 5 is an excellent review of the meager information on the effects of alpha, beta, and gamma radiation on nuclear waste forms. Measurable structural damage to the host glass by radiation requires a cumulative dose of about 10^{24} and saturates at 5×10^{26} alpha decays/m³. These doses roughly correspond to 10,000 y exposure. There is a rough correlation between structural damage, which is indicated by an increase in volume, and leach rate for irradiated nuclear waste forms. Gamma radiation passing through the canister is known to interact with air and water to form nitric acid and hydrogen peroxide. More information concerning the concentrations and the effect of these oxidizing species on the corrosion of the canister during the initial 300 y isolation period needs to be obtained.

"Solidification of Savannah River Plant High-Level Waste" is a report that presents a general overview of DWPF history, design, development and operations. The major emphasis of this report is the reduction in volume of high-level waste to be dealt with in the higher cost glass forming process and a significant increase in the amount to be mixed with cement and disposed of as low-level waste [Maher et al. 1983, see Appendix B, p. 73].

A brief review of "Processing of Transuranic Waste at the Savannah River Plant." This report gives a review of the plan for retrieval, reprocessing and final disposal at Carlsbad, New Mexico, of transuranic waste presently stored on the Savannah River Plant site [Daugherty et al. 1987, see Appendix B, p. 66].

An overview of the "Process Technology for Vitrification of Defense High-Level Waste at Savannah River Plant," was completed. The SRP waste exists in three forms: sludge, saltcake, and saturated salt solution. Decontamination procedures of the bulk of the salt solution for disposal as low-level chemical disposal are detailed. Concentration of the remaining radionuclides for vitrification is also described as are preparation of intermediate process by-products, for example Hg. This NIST review does not contain critical commentary by the reviewer but it will be included for reference purposes in the "Database for Reviews and Evaluations on High-Level Waste (HLW) Data" [Boersma 1984, see Appendix B, p. 56].

"Glass Making Technology for High Level Nuclear Waste," was a talk geared toward chemical engineers. It is a good general paper covering the well known problems of SRP high level waste such as removal of mercury from the sludge, the task of removing large amounts of salts, and non-radioactive sludge components from the radioactive waste for disposal as low-level waste, and the vitrification of the remaining high-level waste [Boersma et al. 1986, see Appendix B, p. 60].

A review of was conducted of a paper entitled, "A Method for Showing Compliance with High-Level Waste Acceptance Specifications." This report that discusses the methods that the West Valley Demonstration Project (WVDP) will use to prepare the waste form and show that it will meet DOE specifications. The techniques being developed to meet the specifications will be detailed in the waste compliance plan. Additional documentation of glass composition control and durability of glasses which are off reference composition are needed [Eisenstatt et al. 1986, see Appendix B, p. 69].

In an effort to develop accurate laboratory data on glass waste leaching for use in modeling efforts, a test plan has been developed [Aines 1987, see Appendix B, p. 52]. Information in the following areas is being sought: radionuclide degradation rates, release rates, and solution compositions in contact with the glass. This work is in the planning stage and no data are available at this time.

3.2.3.3 Modeling the Dissolution of Glass Waste

Once the nuclear waste container is breached, dissolution of radionuclides will commence as water or steam contacts the vitrified waste. A geochemical modeling code, EQ3/6, on the dissolution behavior of glass in an aqueous environment is used to evaluate the long-term effects of exposure of glass to a tuff repository environment [Aines 1986, see Appendix B, p. 49]. The model is designed to allow experimental verification at various stages of development. Modifications to EQ3/6 that tailor the existing model to the needs of NNWSI are described in this report. One result of this model is its ability to generate possible scenarios for the dissolution of radionuclides. Presently, EQ3/6 can deal with simple scenarios, but it is not able to generate complex, realistic scenarios because of the lack of sufficient experimental data.

3.2.4 Water Chemistry

A report on water chemistry [Reed and Van Konyenburg 1987] summarizes data given in a literature review on the effect of ionizing radiation on dry and wet nitrogen/oxygen systems. One important reaction product is the nitric acid that is a product of nitrogen fixation. It is expected that the amount of nitric acid that forms will be small relative to the mass of the container. However, as the author points out, condensation in the form of droplets on the metal container may localize the formation of acid. The confinement of the acid to these droplets would lead to a higher concentration of acid than would otherwise be expected. A less likely reaction, the formation of ammonia, requires a reducing environment. It is well known that ammonia can be detrimental for copper-based alloys. Further experimental work is needed in this area. The possible localization of nitric acid condensation is an issue that must be investigated further, since it may lead to localized degradation of the canister.

A second report in this section reviews and evaluates the data on the release of carbon-14 from spent fuel into the environment by gaseous transport [Van Konyenburg et al. 1986]. The review discusses the possible modes of release of ^{14}C from the repository and puts it in the context of concentrations of natural occurring ^{14}C . However, because of a lack of measured data, it is difficult to predict the rate of oxidation and release of ^{14}C from a repository environment.

4.0 MCC -- Materials Characterization Center

The Materials Characterization Center (MCC) is a Department of Energy (DOE) laboratory which was organized for the purpose of ensuring that qualified materials data are available on nuclear waste materials. The MCC is located in the state of Washington and operated by the Pacific Northwest Laboratories (PNL) of the Battelle Memorial Research Institute.

Originally, objectives were to (1) develop standard test methods and have them approved, (2) test nuclear waste materials using approved test methods and (3) publish test procedures and data in the Nuclear Waste Materials Handbook. Approved test materials (ATM) and reference materials would be developed and held by the MCC and provided for use as needed. The Materials Review Board (MRB), which was to review and approve the test methods and data, has been abolished. The plan now is to have the test methods and data undergo peer review. Changes may occur in the objectives of the MCC.

The MCC is supported at a level of approximately 60 percent as direct support from the DOE, and the remainder of the funding comes from DOE offices that deal with nuclear waste materials and nuclear waste storage and have work for the MCC to do. The MCC prepares monthly reports in addition to other project reports which are submitted to the supporting offices.

The sections of the monthly reports for January through June, 1988 were as follows. The MCC work in each of these sections will be summarized. See Appendix D for the details.

- A. Program Administration
- B. Quality Assurance
- C. Support to the Office of Geologic Repositories, through April, 1988
Support to the Office of Facilities Siting and Development, beginning May 1, 1988.
- D. Support to the Salt Repository Project
- E. Support to the Basalt Waste Isolation Project
- F. Support to the Defense HLW Technology Program
- G. Defense Waste Processing Facility
- H. Support to the West Valley Demonstration Project

Appendix A. Waste Package Data Review Form Guidelines

Appendix A

Waste Package Data Review Form Guidelines

DATA SOURCE

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

TECHNICAL REPORT:

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

CONFERENCE PAPER:

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

DATE REVIEWED

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

PURPOSE

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

CONTENTS

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

TYPE OF DATA

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

MATERIALS/COMPONENTS

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

TEST CONDITIONS

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

METHODS OF DATA COLLECTION/ANALYSIS

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

AMOUNT OF DATA

This section includes the number of tables and graphs together with their titles and axes (including the range in values). If a listing of figure and table titles is provided, the reviewer should add the limits given on each axis, i.e. for temperature, or other explanatory information as appropriate.

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

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

UNCERTAINTIES IN DATA

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

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

DEFICIENCIES/LIMITATIONS IN DATABASE

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

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

KEY WORDS

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

CONCLUSIONS

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

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 certain workers in this area, this review still considers a sufficiently large number of other investigations to provide a good understanding of the present status of the field. The principal deficiency, however, is the omission of stainless steel types, 301, 303, 304, and 316 and studies at 440°C.

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

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

RECOMMENDATIONS

Especially list what additional tests should be conducted or what types of additional data are needed to resolve selected issues or questions. Any newly identified problems will be used to update a list of NBS identified materials problems that includes statements on the types of additional data, models, etc. that are needed to answer outstanding questions.

RELATED HLW REPORTS

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

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

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

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

The ranking of the paper is determined as follows: The "Key Data" box is marked if the paper contains data that is of sufficient quality that it must be considered by NRC in an evaluation of a license application. Such a paper must meet at least one of the following criteria: (1) it is an in-depth review of the pertinent literature, (2) it contains data that is found to be especially significant after being assessed for scientific merit and quality, or (3) it contains data with such a small uncertainty that it must be considered in a performance evaluation of a license application. If the paper does not meet any of the above three criteria, it is indicated as "Supporting Data".

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

AUTHOR'S ABSTRACT

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

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

Appendix B

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

	Page
Aines, R. D., "Application of EQ3/6 to Modeling of Nuclear Waste Glass Behavior in A Tuff Repository," UCID-20895, May 1986	B-49
Aines, R. D., "Plan for Glass Waste Form Testing for NNWSI," UCID-21190, September 1987	B-52
Boersma, M. D., "Process Technology for Vitrification of Defense High-Level Waste at the Savannah River Plant," DP-MS-83-135, August 26-29, 1984	B-56
Boersma, M. D. and Mahoney, J. L., "Glass Making Technology for High Level Nuclear Waste," DP-MS-86-75, August 24-27, 1986	B-60
Bullen, D. B., Gdowski, G. E., and McCright, R. D., "Impact of Phase Stability on the Corrosion Behavior of the Austenitic Candidate Materials for NNWSI," UCRL-97562, October 1987	B-5
Daugherty, B. A., Salizzoni, L. M., and Mentrup, S. J., "Processing of Transuranic Waste at the Savannah River Plant," DP-MS-86-48, March 1987	B-66
Delany, J. M., "Reaction of Topopah Spring Tuff with J-13 Water: A Geochemical Modeling Approach Using the EQ3/6 Reaction Path Code," UCRL-53631, November 1985	B-11
Eisenstatt, L. R., Chapman, C. C., and Bogart, R. L., "A Method for Showing Compliance with High-Level Waste Acceptance Specifications," Waste Management '86, University of Arizona, Tucson, Arizona 1986.	B-69

	Page
Glass, R. S., Overturf, G. E., Van Konynenburg, R. A., and McCright, R. D., "Gamma Radiation Effects on Corrosion: I - Electrochemical Mechanisms for the Aqueous Corrosion Processes of Austenitic Stainless Steels," UCRL-92311, February 1986 . . .	B-18
Maher, R., Shafranek, L. F., and Stevens, W. R., "Solidification of Savannah River Plant High-Level Waste," DP-MS-83-110, November 1983 . . .	B-73
McCright, R. D., Haisey, W. G., and Van Konynenburg, R. A., "Progress Report on the Results of Testing Advanced Conceptual Design Metal Barrier Materials Under Relevant Environmental Conditions for a Tuff Repository," UCID-21044, December 1987.	B-23
Mendel, J. E., "Final Report of the Defense High-Level Waste Leaching Mechanisms Program," Chapter 2, Surface Layers in Leached Borosilicate Glass High-Level Defense Nuclear Waste Forms, PNL-5157, August 1984	B-76
Mendel, J. E., "Final Report of the Defense High Level Waste Leaching Mechanisms Program," Chapter 5, Radiation Effects, PNL-5157, August 1984	B-86
Reed, D. T. and Van Konynenburg, R. A., "Effect of Ionizing Radiation on Moist Air Systems," UCRL-97936, December 1987	B-31
Smith, D. H., "The Influence of Copper on Zircaloy Spent Fuel Cladding Degradation Under a Potential Tuff Repository Condition," UCRL-15993, SANL 622024, March 1987	B-91
Van Konynenburg, R. A., Smith, C. F., Culham, H. W., and Smith, H. D., "Carbon-14 in Waste Packages for Spent Fuel in a Tuff Repository," UCRL-94708, October 1986	B-34

	Page
Westerman, R. E., Pitman, S. G., and Haberman, J. H., "Corrosion Testing of Type 304L Stainless Steel in Tuff Groundwater Environments," UCRL-21005, SANL 616-007, November 1987	B-38
Wilson, C. N., Einziger, R. E., Woodley, R. E., and Oversby, V. M., "LWR Spent Fuel Characteristics Relevant to Performance as a Wasteform in a Potential Tuff Repository," UCRL-92891, June 1985	B-95

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

Bullen, D. B., Gdowski, G. E., and McCright, R. D., "Impact of Phase Stability on the Corrosion Behavior of the Austenitic Candidate Materials for NNWSI," UCRL-97562, October 1987. Available from NTIS.

DATE REVIEWED: 4/18/88; Revised 6/30/88.

PURPOSE

To review the technical literature regarding phase stability of 304L, 316L and the Alloy 825 and to summarize the role of phase stability on the degradation of these materials in the repository environment.

Comment: In reality, it appears that phase metastability is reviewed.

CONTENTS

10 pages with one table, six figures 32 references.

TYPE OF DATA

A review article.

MATERIALS/COMPONENTS

304L stainless steel, 316L stainless steel and Alloy 825

TEST CONDITIONS

No tests were conducted. Test conditions in the literature reviewed included high temperature studies and phase transformations. Conditions of composition, temperature of exposure, temperature at quenching and previous history of mechanical or thermomechanical treatment are identified as important to the austenite to martensite transformation and to other transformations.

METHODS OF DATA COLLECTION/ANALYSIS

Light microscopy, electron microscopy, and x-ray diffraction were used in articles surveyed for this review.

AMOUNT OF DATA

One table gives compositions of 304, 304L, 316 and 316L stainless steels and Alloy 825. Six figures present the Fe-Cr-Ni ternary phase diagram at 650°C, two metastable phase diagrams for quenched Fe-Cr-Ni alloys, the effect of carbide precipitation on intergranular corrosion, the effect of sigma phase formation on room-temperature impact strength, a time-temperature precipitation diagram for 316 SS, and cross-sections of the Fe-Cr-Ni ternary phase diagram.

Iron melts at 1539°C. From 1539°C to 1390°C, iron has a body-centered cubic (bcc) structure, δ ferrite, and a face-centered cubic (fcc) structure, austenitic γ iron, from 1390°C to 910°C. Below 910°C, iron exists as bcc α ferrite. Above 13% Cr, ferrite is stable at all temperatures. Mo, Si, Al, Ti and Nb, like Cr, reduce the austenite area on the phase diagram, whereas Ni, Mn, Cu and Co increase carbon and nitrogen solubility and austenite stability.

Austenitic steels all contain more than 16% Cr, and therefore 304L and 316L SS should contain a ferrite phase in equilibrium with austenite at 200°C. Its precipitation is hindered by the slowness of the diffusion processes required to create it. Thus, the austenite phase is stable for 10 to 40 years, but may not be over much longer time. Austenite can also transform to martensite upon cold working.

Martensite can exist as α' (bcc) or ϵ (hexagonal close packed). The latter appears to be an intermediate phase in the formation of α' . Low-alloy fcc austenites transform to α' martensite at or below room temperature. Martensite is harder and more brittle than austenite, and is more susceptible to hydrogen embrittlement.

Carbide precipitation is possible even for low carbon austenite iron alloys. Some elements, such as Ti, are strong carbide formers. Carbides such as $M_{23}C_6$ also can form in equilibrium with the carbides of the strong carbide formers and carbon is ubiquitous in their absence. The carbide precipitation initially occurs at grain boundaries. Stickler and Vinckier found that $M_{23}C_6$ precipitates initially at austenite-ferrite interfaces and is followed by carbide precipitation at grain boundaries. Given sufficient carbon, $M_{23}C_6$ can form at temperatures as low as 400°C after 1500 hours, or within a minute at 900°C. Intergranular corrosion following $M_{23}C_6$ precipitation occurs below 750°C.

Austenitic steels can also form intermediate phases (over the temperature range 600-1150°C) whose composition may be stoichiometric or may exhibit a range. The tetragonal sigma phase may range from A_4B to AB_4 . The chi phase has a bcc- α Mn structure with a formula $(FeNi)_{36}Cr_{12}Mo_{10}$. The hexagonal Laves phase has the formula Fe_2Mo . Less than 2% sigma phase reduces the fracture toughness by half. Overall, the studies outlined show that 304L and 316L steels can undergo significant microstructural evolution at temperatures less than 650°C in less than 1000 hours.

Alloy 825 is a stable austenite over the entire range from the solidus temperature to room temperature. Also, the precipitation of sigma, chi, or Laves phases has not been noted in the literature. However, a wide variation in resistance to sensitization has been observed that is attributed to differences in process history.

UNCERTAINTIES IN DATA

The uncertainties discussed are paraphrased from the authors by the reviewer. The metastable austenitic phase should be in equilibrium with the ferritic phase at 200°C, the austenitic phase is metastable. This austenitic microstructure is known to be stable for up to 40 y at amount temperatures of 0 to 40°C but its stability is not known for 1000 y under repository conditions. Transformation of austenite to martensite due to effects of temperature, strain, or composition can occur with 304L and 316L stainless steel. This transformation could adversely affect mechanical properties. The precipitation of carbides, predominately $M_{23}C_6$, at grain boundaries could occur after long periods of time, and this would affect the corrosion and mechanical properties. The formation of intermediate phases such as the sigma phase can result in reduced fracture toughness. Long hold times, at repository temperatures or even during the time period for container retrieval, could cause precipitation of these phases or carbides, and all low-temperature phase transformations should be considered when selecting the material.

Speculation regarding the possible existence of submicroscopic sigma phase in the Alloy 825 was noted but not substantiated with data.

DEFICIENCIES/LIMITATIONS IN DATABASE

Data are needed on long-term, low-temperature (below 650°C) phase transformations for all of the phases.

KEY WORDS

Literature review, supporting data, microscopy, x-ray diffraction, electron microscopy, ambient temperature, high temperature, stainless steel, austenitic alloys, 304L stainless steel, 316L stainless steel, Alloy 825, annealed (austenitized and transformed), sensitized, impact strength, corrosion (galvanic), corrosion (intergranular), corrosion (stress cracking), cracking, cracking environmentally assisted, hydrogen embrittlement, sigma phases, chi phase, Laves phase, intermetallic phase, carbides.

CONCLUSIONS

"Types 304L and 316L stainless steels were identified as potentially metastable materials at repository relevant conditions."

This is not a new conclusion, however. Diffusion processes needed for precipitation reactions, occur slowly at temperatures below 650°C, and the predicted maximum repository temperature of 250°C is significantly lower.

"Carbide precipitation was identified in all of the austenitic candidate alloys."

Carbide precipitation may lead to sensitization in 304L and 316L and the potential for intergranular stress corrosion cracking.

Intermetallic phases such as sigma, chi and Laves, were noted to occur in 316L. These phases result in brittleness and reduce the impact strength. However, "No intermetallic phases formation was documented in Alloy 825," and "Very few phase instability data were identified for Alloy 825."

Limited data were available on $M_{23}C_6$ carbide precipitation in the Alloy 825 and varying compositions of the carbide in the Alloy 825 were reported.

GENERAL COMMENTS OF REVIEWER

This document is an excellent review of phase stability in austenitic candidate materials, covering a number of topics relevant to the NNWSI Project studied. However, none of the material in the review addresses the role of phase stability in the degradation of the materials discussed in a repository environment. Attention should be given to items mentioned in the sections of this review entitled comments, uncertainties in data, and conclusions.

The phase stability of 304L and 316L stainless steels at repository temperatures is questionable and must be resolved. Although diffusion reactions would be slower at 250°C than at 650°C, the time of exposure is long for repository conditions, and ferritic phase would precipitate at the lower temperatures. More data on effects of composition, temperature, time and deformation on phase stability of these materials are needed. It is not clear whether the forty year successful use of these materials could furnish useful data for repository conditions or if it does, whether this time period could be greatly extended. This stability question may not lend itself to a resolution, and the question that must be raised is should metastable materials be used in the engineered barrier.

The review indicates that Alloy 825 is more promising than the stainless steels, but much more data are needed on carbide and other possible phase formations in this material. These data should be correlated with mechanical properties and assessed in relation to temperature, time and repository conditions. The review relates phase instability to intergranular stress corrosion cracking. There are additional corrosion problems, such as pitting or galvanic corrosion, which could occur.

Recommendations related to this work include:

1. Evaluate the generic question whether metastable materials should be used in the waste packages.
2. Make additional studies of phase stability of austenitic materials.
3. Study carbide precipitation in 304L, 316L and the Alloy 825 under temperatures involved in preparing the canister for storage and temperatures that will exist in the repository. Consider effects of long-time exposures.
4. Study effects of carbon content and the total alloy composition on carbide precipitation in candidate austenitic materials at temperatures of preparation and storage in the repository waste packages.
5. Study intermetallic phase formation and effects of temperature, time and composition for 304L, 316L and Alloy 825.
6. Analyze combined effects of gamma radiation and repository temperatures on phase stability of austenitic materials.
7. Correlate measurements of mechanical properties and corrosion behavior with phase change data.

RELATED HLW REPORTS

McCright, R. D. Halsey, W. G., Van Konynenburg, R. A.
"Progress Report on the Results of Testing Advanced Conceptual
Design Metal Barrier Materials Under Relevant Environmental
Conditions for a Tuff Repository"
UCID-21044, December, 1987.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.2.3 Possible mechanical failure modes for waste package

2.2.4 Potential corrosion failure modes for the waste package.

(b) New Licensing Issues

Sensitization and/or phase stability of austenitic materials

(c) Comments Related to licensing

Effects of phase metastabilities on mechanical properties, corrosion behavior and overall durability of austenitic materials need to be determined. A material should be used only if it can be established that phase transformation and their effects do not limit the integrity of the container in the repository environment over the needed containment time.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

Delany, J. M., "Reaction of Topopah Spring Tuff with J-13 Water: A Geochemical Modeling Approach Using the EQ3/6 Reaction Path Code," UCRL-53631, November 25, 1985.

DATE REVIEWED: 5/21/88; Revised 6/13/88; 7/17/88.

PURPOSE

To investigate the usefulness of the EQ3/6 geochemical modeling code as a tool to reproduce theoretically the physical/chemical environments of the NNWSI waste package.

CONTENTS

The report consists of 46 pages.: four tables, six figures, three appendices, and a bibliography of 54 references. There are a general description of the EQ3/6 software, the code input parameters, discussion of four different computer simulations and the results. Experimental data characterizing the J-13 well water and the bulk mineralogy of the Topopah Spring Tuff are discussed.

TYPE OF DATA

(1) Scope of the Report

Description of EQ3/6 Reaction Path Code; a comparison of specific experimental data (taken from UCRL-53630 and UCRL-53645) with the results of computer modeling of the reaction of Topopah Spring tuff with J-13 groundwater.

(2) Failure Mode or Phenomenon Studied

Dissolution of Topopah Spring Tuff in J-13 groundwater over time (computer simulation).

MATERIALS/COMPONENTS

Topopah Spring Tuff from Drill hole USW G-1 at 1232 feet.

J-13 groundwater from USGS Test Well 6 1963.

TEST CONDITIONS

(1) State of the Material being Tested

In the quoted experimental work:

Tuff was tested in both crushed and wafer forms.

J-13 groundwater from USGS Test Well 6 1963, stored in a plastic-lined drum filled directly at the well. Storage conditions do not significantly affect overall composition, but tests indicated that the storage tank became saturated with oxygen and the pH rose from 7.1 to 7.6 during storage.

(2) Specimen Preparation

In the quoted experimental work:

1. Crushed samples of tuff were dry-sieved to a size range of 75 to 150 μm . The samples were unwashed and probably contained fine particulate material.
2. Core-wafer samples were cut, polished, washed thoroughly in distilled water, and cleaned in an ultrasonic bath to remove all fine particles from the surfaces; effective porosity 6.5%, measured bulk density 2.335 g/cm^3 , grain density 2.522 g/cm^3 .

(3) Environment of the Material being Tested

In the experimental work quoted, the tests of tuff reacting with J-13 water were run at 150 and 250°C.

METHODS OF DATA COLLECTION/ANALYSIS

The laboratory data were gathered by other workers at Lawrence Livermore National Laboratory. Details are not given in this report except that the experiments were run at 150 and 250°C for 66 days on the samples described above.

Geochemical modeling was done using the EQ3/6 reaction path code to model the complex chemical interactions between groundwater and repository host rock. The EQ3/6 code consists of two large FORTRAN codes which are supported by a common thermodynamic database. One code is a speciation-solubility code that computes a model of the state of an aqueous solution. The program produces the distribution of aqueous species, their thermodynamic activities and saturation indices for various solids. The second program can be used to compute models of the evolution of aqueous geochemical systems (the reaction path). Changes in rock/water systems are calculated as the reactions proceed toward a state of overall chemical equilibrium. The thermodynamic data are processed through a code which checks for thermodynamic consistency, extrapolates heat capacity functions with temperature, and generates data for insertion into the master thermodynamic data file. The internal database contains free energies and enthalpies of formation, third law entropies, and heat capacities of reactions commonly used in geochemical calculations. The program also checks for mass and charge balance, fits all data to a predetermined temperature grid.

This report describes the application of the codes to help evaluate chemical reactions occurring in closed-system high-temperature experiments. The interaction between tuff and J-13 water is modeled as the reaction of an aqueous solution in contact with a specific mineral assemblage. The bulk-rock mineralogy was represented as an assemblage of cristobalite, alkali feldspar, and quartz with minor amounts of biotite, plagioclase, and montmorillonite. Analyses of natural J-13 water served as direct input for the composition of the initial fluid. The EQ6 code predicts the reactions of the rock and water compositions at the experimental temperatures for the designated time intervals. The reaction products produced by the EQ6 code were compared with experimental data.

AMOUNT OF DATA

There are four tables and six figures in the main body of the test and three appendixes.

Table 1.: "Average J-13 fluid analysis for LLNL laboratory supply," lists the pH, and the concentration in milligram/liter for 14 ions in the water.

Table 2.: "Composition of Topopah Spring tuff," lists six mineral phases by name, by mineral composition, and the volume percent of each mineral in the tuff.

Table 3a.: "EQ6 rock recipe for crushed Topopah Spring Tuff," lists for six mineral species, the weight percent, the moles of reactant in moles/gram, the initial number of moles of reactant, the specific surface area in square centimeters/gram, and the total surface area in square centimeters.

Table 3b.: "EQ6 rock recipe for G-1 Topopah Spring Tuff core wafer," lists for six mineral species, the weight percent, the moles of reactant in moles/gram, the initial number of moles of reactant, the specific surface area in square centimeters/gram, and the total surface area in square centimeters.

Table 4.: "Steady state J-13 composition (open system 150°C, 100 years; see text)," lists the pH and the concentration in milligrams/liter for 11 ionic components.

Figure 1.: "Log activity plot of potassium vs aqueous silica at 25°C (see text). The open squares represent J-13 compositions from various literature sources. The crosses represent concentrations of the LLNL laboratory supply." Log activity a_{K^+}/a_{H^+} (from 0 to 6) is plotted against log activity a_{SiO_2} (from -6 to 0) with five mineral areas identified in the plot.

Figure 2.: "Log activity plot of sodium vs aqueous silica at 150°C. See Figure 1 for symbol explanation." Log activity a_{Na^+}/a_{H^+} (from 2 to 8) is plotted against log activity a_{SiO_2} (from -6 to 0) with six mineral areas identified in the plot.

Figure 3a.: "Concentration of Si and Na vs time for 150°C Topopah Spring Tuff (Tpt) core-wafer simulation. Symbols represent analytical values from Knauss et al. (1985b)." The concentration in ppm (from 0 to 140) is plotted against the time in days (from 0 to 70).

Figure 3b.: "Concentration of Ca, K, Al, and Mg vs time for 150°C Tpt core-wafer simulation." The concentration in ppm (from 0 to 12) is plotted against the time in days (from 0 to 70).

Figure 4a.: "Concentration of Si and Na vs time for 250°C Tpt core-wafer simulation. Symbols represent analytical values from Knauss et al. (1985b)." The concentration in ppm (from 0 to 400) is plotted against the time in days (from 0 to 70).

Figure 4b.: "Concentration of Ca, K, Al, and Mg vs time for 250°C Tpt core-wafer simulation." The concentration in ppm (from 0 to 14) is plotted against the time in days (from 0 to 70).

Figure 5a.: "Concentration of Si and Na vs time for 150°C Tpt Crushed -tuff simulation. Symbols represent analytical values from Knauss et al. (1985a)." The concentration in ppm (from 20 to 160) is plotted against the time in days (from 0 to 70).

Figure 5b.: "Concentration of Ca, K, Al, and Mg vs time for 150°C Tpt crushed-tuff simulation." The concentration in ppm (from 0 to 14) is plotted against the time in days (from 0 to 70).

Figure 6.: "Concentration vs time plot for 150°C Tpt core-wafer 100-year simulation." Concentrations in ppm (from 0 to 200) of Si, Na, Al, and Ca are plotted against time in years (from 0 to 100).

Appendix A.: "Constants used to construct theoretical rock recipes," lists the numerical values of the densities and molecular weights for six mineral species.

Appendix B.: "Sample EQ3NR Input File of J-13 Water," lists the parameters and the values used in the computer simulations.

Appendix C.: "Sample EQ6 Input File for Core-Water Experiment," lists the data used in the run at 150°C.

UNCERTAINTIES IN DATA

Uncertainties in the experimental data are not given in this report.

DEFICIENCIES/LIMITATIONS IN DATABASE

It is not possible to analyze the alteration products of the crushed-tuff experiments in the same detail possible in the core-wafer experiments. In the core-wafer experiments only a negligible amount of the solids appear to have reacted and so the concentrations of major cations in solution are a sensitive measure of the course of the reaction. Only if good agreement is found between the progressive changes in the theoretical and analytical solution compositions can the EQ6 results be interpreted to predict the secondary alteration that may form in these experiments.

"There is a lack of complete thermodynamic data and also a lack of some of the specific data for species dissolution, for instance, data on the dissolution of smectite phases."

KEY WORDS

Data Analysis, computer modeling, solubility, EQ3/6, laboratory, J-13 water, tuff composition, tuff, dissolution.

CONCLUSIONS

"The dissolution of Topopah Spring tuff in J-13 water may be reasonably approximated" [Ed. reasonable approximation is not defined] in a closed-system environment at 150°C can be simulated with a minimum number of constraints in code parameters but the simulation does not work equally well at 250°C. [Ed. This gives rise to two implications: (1) the actual reaction taking place at 250°C may differ from that of 150°C. (2) The method of numerical analysis used at 150°C may not apply at 250°C]. Future work must include more data on various mineral compositions. The addition of several rate laws for precipitation kinetics will be made to the EQ3/6 software."

GENERAL COMMENTS

The validity of the original data being used in modeling must always be a weak point. For instance, the rate constants for dissolution of an individual mineral component, determined experimentally for that component by itself, may not be valid for the component in association with other mineral phases. Also, the assumptions concerning the identity of all mineral species in the tuff rock may not be inclusive enough. The uncertainty of the data is difficult to estimate. The dependence of the results of modeling on the validity of the assumptions made about any complex system is another weakness.

The author herself states that although the data for experiments at 150°C agree well with the modeling results, the results at 250°C indicate that the database cannot adequately model the system at the higher temperature. The modeling results validate the modeling procedures but the database needs expansion. Too much of the database must consist of estimated thermodynamic values and better data must be inserted in the database.

RELATED HLW REPORTS

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

APPLICABILITY OF DATA TO LICENSING

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

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

This report relates to NNWSI ISTP issue 2.3.2.1.2, the rates of dissolution associated with the potential waste form dissolution mechanisms.

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

Glass, R. S., Overturf, G. E., Van Konynenburg, R. A., and McCright, R. D., "Gamma Radiation Effects on Corrosion: 1 - Electrochemical Mechanisms for the Aqueous Corrosion Processes of Austenitic Stainless Steels," UCRL-92311, February 1986. Available from NTIS.

DATE REVIEWED: 3/16/88; Revised 6/8/88.

PURPOSE

Determine the effects of gamma irradiation with the addition of H_2O_2 on the electrochemical behavior of austenitic stainless steels.

TYPE OF DATA

Experimental.

MATERIALS/COMPONENTS

304L and 316L SS, annealed.

TEST CONDITIONS

J-13 and concentrated J-13 groundwater, with and without γ -radiation, $T = 30^\circ C$.

METHODS OF DATA COLLECTION/ANALYSIS

Open circuit potentials and polarization curve.

AMOUNT OF DATA

Tables

1. Composition of the metal.
2. Composition of the J-13 water.
3. Possible redox reactions in γ -irradiation solution.

Figures

1. Schematic of the electrochemical cell used.
2. Corrosion potential behavior of 316L stainless steel in 10x concentrated J-13 well water under gamma irradiation. The solution was not exposed to irradiation prior to initiation of the first "on/off" irradiation cycle.
3. As for Figure 2, only for a 100x concentrated J-13 electrolyte.
4. Open circuit potential of 316L as a function of time (up to 600 min), showing the effect of γ -radiation and of H_2O_2 addition.
5. Response of the corrosion potential for 316L stainless steel in J-13 well water to which successive additions of H_2O_2 were made. In this figure, one drop of H_2O_2 (from a 30% solution) represents a resulting solution concentration of 0.49 mM. The solution was continuously stirred by a magnetic stirrer throughout the experiment.
6. Open-circuit potential behavior for platinum irradiated J-13 well water.
7. Same as Figure 6, only with continuous purging of the solution by argon throughout the experiment.
8. Response of the open-circuit potential for platinum unirradiated J-13 well water to successive additions of H_2 , H_2O_2 , and O_2 . The points of introduction of these species into solution are indicated on the figure. In this figure, two drops of H_2O_2 (from a 30% solution) results in a solution concentration of 0.98 mM. Purging of the solution with H_2 and O_2 resulted in successive saturated solutions of these gases. The solution was continuously stirred by a magnetic stirrer during the experiment.
9. Response of the corrosion potential for 316L stainless steel in J-13 well water to successive additions of H_2O_2 and H_2 . The points of introduction of these species into solution are indicated on the figure. In this experiment the addition of two drops of H_2O_2 (from a 30% solution) results in a solution concentration of 0.98 mM. Purging of the solution with solution with H_2 . The solution was continuously stirred with a magnetic stirrer in this experiment.
10. Response of the corrosion potential for 316L stainless steel in argon-purged J-13 well water to gamma irradiation. Initiation of argon deaeration and gamma irradiation are indicated on the figure. Once initiated, argon purging was continued throughout the remainder of the experiment.

11. Comparison of the potentiostatic anodic polarization behavior for 316L stainless steel in 650 ppm Cl^- solution in deionized water with and without gamma irradiation. The polarization curves were scanned anodically starting from the corrosion potential in each case. Upon reaching the anodic limit, the scans were reversed to more negative potentials. In this figure, E_{CORR} and E_p represent values of the corrosion potential and pitting potential, respectively, for the unirradiated case. The corresponding values for the irradiated experiment are indicated on the figure as $*E_{\text{corr}}$ and $*E_p$.

UNCERTAINTIES IN DATA

None given. Results of single experiments.

DEFICIENCIES/LIMITATIONS IN DATABASE

Considered preliminary results by the authors.

KEY WORDS

316L SS, J-13 water, γ -irradiation, corrosion.

CONCLUSIONS

1. "Gamma irradiation increases the oxidizing nature of the aqueous solutions used in this study through production of $\bullet\text{OH}$ and H_2O_2 . These species probably account for the observed positive corrosion potential shifts. Such shifts may be generic for austenitic stainless steels in J-13 well water and in similar environments."
2. "By analogy to previous work on Pt in aqueous H_2O_2 media, the electrochemical equilibrium between adsorbed hydroxyl species and hydroxide ions may be important in determining the corrosion potentials of stainless steel in irradiated aqueous solutions. Also a cyclical catalytic scheme for the decomposition of H_2O_2 involving adsorbed species (e.g., $\bullet\text{OH}$, HO_2 , or O_2) participating in anodic and cathodic processes may also be important. However, a stainless steel surface certainly forms a more complex electrochemical interface than does a Pt surface, and other reactions also serve to establish a mixed corrosion potential, as discussed in the text."
3. "The generation of oxidizing species in the solution layers adjacent to the stainless steel surface is responsible for the rapid potential shifts observed upon imposition of the gamma field. Upon continued

radiolysis, a rise in concentration of oxidizing species (particularly H_2O_2) in the bulk solution also gradually increases the steady-state corrosion potential of the stainless steel."

4. "The corrosion potential of 316L stainless steel, while sensitive to the presence of H_2O_2 , does not appear to be sensitive to the presence of H_2 under our experimental conditions. While the corrosion potential is not sensitive to molecular H_2 , it may be sensitive to atomic hydrogen, which is also produced under radiolysis. Molecular hydrogen may only play a role in helping to establish steady-state bulk H_2O_2 concentrations."
5. "Preliminary results suggest that the susceptibility of 316L stainless steel to pitting is not increased under gamma irradiation. It appears that both the corrosion and pitting potentials are shifted positively by approximately the same amount. The more positive pitting potentials observed under gamma irradiation may be related to reaction of radiolytic products with defects (e.g., oxygen vacancies) in the oxide film, or to film-repair reactions. Further work is needed to understand the effect of gamma irradiation over wide ranges of the polarization curves."

GENERAL COMMENTS OF REVIEWER

Although data are very limited and preliminary, they are in general agreement with the expected effects of γ -irradiation. The discussion concerning the reactions and mechanisms that alter the corrosion potential of stainless steel under γ -irradiation, is reasonable, but it must be emphasized that it is highly speculative. Finally, the results of a single potentiodynamic scan are interpreted as indicating no detrimental effect of γ -radiation on pitting. However, the fact that the repassivation potential seems to be below the open circuit potential under irradiation could very well mean that if pitting were initiated for whatever reason, no spontaneous repassivation and pit death (pit deactivation) would be expected.

RECOMMENDATIONS

None.

RELATED HLW REPORTS

Reed, D. T. and Van Konynenburg, R. A., "Effect of Ionizing Radiation on Moist Air Systems," UCRL-97936, December 1987.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to 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 Nuclear Regulatory Commission regulations for geologic disposal of high level nuclear wastes require multibarriered packages for waste containment that are environmentally stable for time periods of 300 to 1000 years. In addition to examining the usual corrosion failure modes which must be evaluated in choosing a corrosion resistant material for waste containment (e.g., resistant to pitting, crevice attack, and stress-corrosion cracking), the effects of gamma radiation on the chemical environment surrounding the waste container must also be considered. Austenitic stainless steels have been proposed for use as waste container materials for a potential nuclear repository to be located at Yucca Mountain in Nye County, Nevada. This study focuses on the effects of gamma radiation on the corrosion mechanisms of 316L stainless steel in groundwater regional to this site. When gamma irradiation is initiated, corrosion potential shifts in the positive direction are observed for 316L in groundwater regional to the repository site. These potential shifts, as well as the subsequent effect on pitting resistance are considered.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

McCright, R. D., Halsey, W. G., and Van Konynenburg, R. A., "Progress Report on the Results of Testing Advanced Conceptual Design Metal Barrier Materials Under Relevant Environmental Conditions for a Tuff Repository," UCID-21044, December 1987.

DATE REVIEWED: 3/31/88; Revised 4/28/88.

PURPOSE

"This report discusses potential degradation modes for candidate materials being considered for use in waste package containers, and summarizes the results of metal barrier testing activities conducted at LLNL and subcontractor facilities."

CONTENTS

This report consists of 105 pages which include an executive summary, an introduction, 16 Tables, 17 Figures, and the following number of pages covering each topic listed.

<u>Topic</u>	<u>Pages</u>
Candidate Materials	5
Degradation Modes of Austenitic Materials Under Repository Conditions	11
General Corrosion and Oxidation of Austenitic Materials	6
Intergranular Corrosion and Intergranular Stress	19
Corrosion Cracking of Austenitic Materials Pitting Corrosion, Crevice Corrosion, and Transgranular Corrosion Cracking of Austenitic Materials	21
Phase Stability and Embrittlement of Austenitic Materials	5
Projections of Containment Lifetimes Using Austenitic Materials	6

<u>Topic</u>	<u>Pages</u>
Copper Base Materials	17
Borehole Liner Materials	3
References	7

TYPE OF DATA

Experimental. This is a review of repository conditions, emplacement considerations and potential degradation modes of six materials and summarizes test data from LLNL and other DOE contractor facilities. Tables and figures of some referenced experimental test data are given.

MATERIALS/COMPONENTS

Six candidate materials for the waste package are discussed. The materials are AISI 304L and 316L stainless steels, high nickel austenitic alloy 825, oxygen-free copper CDA 102, 7% aluminum bronze CDA 615, and 70-30 copper-nickel, CDA 715.

TEST CONDITIONS

Topopah Spring tuff repository conditions were used in the various tests. These conditions included J-13 well water with a near neutral pH and temperatures of 28°C to 150°C. Some tests were conducted in the presence of gamma radiation at approximately 10^4 to 10^5 rads per hour.

METHODS OF DATA COLLECTION/ANALYSIS

Weight loss measurements were used to determine corrosion rates and effects of composition and other variables. Slow-strain-rate tests were conducted to obtain data on changes in mechanical properties brought about by the environment. U-bend SCC tests were conducted. Metallographic techniques, using light microscopy, were used to analyze microstructures for cracking and other effects.

AMOUNT OF DATA

There are 16 tables and 17 figures.

UNCERTAINTIES IN DATA

It is not certain whether sensitization would occur during the tens to hundreds of years at 100°C to 250°C in the repository.

In the transgranular SCC determinations, tuff material was taken from surface outcroppings and was not representative of the tuff at the level of the repository. Total volumes of water were not kept constant throughout the test and resulted in varying chloride concentration. Temperatures were not controlled satisfactorily at 90°C for the first month which resulted in a more concentrated solution. A peak value of chloride was measured after seven months.

DEFICIENCIES/LIMITATIONS IN DATABASE

Partial sensitization might occur and needs to be quantified. Additional slow-strain-rate tests are being conducted. A model to predict sensitization is being developed. Detrimental effects of hydrogen on Alloy 825 need to be addressed. Additional work is needed to study phase instability and embrittlement. More developmental work is needed with Alloy 825 to assure its good weldability. More research is needed to determine whether microorganisms can survive the hot, dry period and later revive. More information is needed on radiation effects on corrosion and oxidation of copper and copper alloys. Interaction of borehole materials and the container will need to be experimentally determined.

KEY WORDS

Experimental, literature review, supporting data, general corrosion, pitting, corrosion, electrochemical, irradiation-corrosion test, microscopy, slow-strain-rate test, weight change, x-ray diffraction, laboratory, simulated field test, Yucca Mountain, air, J-13 water, tuff composition, concentrated (20X) J-13 water, tuff gamma radiation field, high temperature, carbon steel, copper base, nickel base, stainless steel, weld, 304L stainless steel, 316L stainless steel, Alloy 825, CDA 102 copper, CDA 613 7% Al-Cu bronze, CDA 715 70-30 Cu-Ni alloy, annealed, sensitized, welded, wrought, slow strain rate, C-ring SCC, J-13 steam, chloride (low ionic content), chloride (high ionic content), tuff, cracking, hydrogen embrittlement, sensitization.

CONCLUSIONS

There is no Conclusions section in this report. Some of the authors' summary statements are discussed in the general comments section of this review. Some assumptions and comments, mostly from the executive summary, follow.

1. Austenite in 304L and 316L stainless steels is metastable and might transform to martensite, ferrite,

sigma or to other phases causing a reduction in fracture toughness and an increased tendency toward mechanical failure.

2. All welded joints except the final closure will be annealed to relieve stress. The final closure could be a point of limitation and this should be resolved.

3. The maximum temperature after closing the repository will be 250°C. The repository will cool eventually and allow condensation or flow of water. Water near the site is low in ionic content and has a neutral pH. The atmosphere will be warm air, steam and cool aqueous air. Gamma radiation will be present and will alter the local environment during the early period.

4. Candidate materials appear to be resistant to corrosive attack to meet performance requirements, but tests indicate that concentration of ionic species could cause more severe pitting attack.

5. Tests on 304 and 304L stainless steel revealed transgranular stress corrosion cracking (TGSCC) under accelerated conditions of stress, gamma flux and water chemistry. Tests are being conducted to quantify critical values and to determine when this corrosion mode becomes limiting.

6. Indications are that phase stability and embrittlement effects will not be performance limiting, but little testing has been done, and further study is being pursued.

7. Testing of the waste package materials is directed toward determining which potential degradation modes are performance-limiting and which degradation modes do not appear to be limiting.

GENERAL COMMENTS OF REVIEWER

This report contains much useful information and addresses many of the scientific questions associated with repository metal barrier systems. However, there are not sufficient data and the data matrices are not developed well enough to make valid conclusions regarding the long term durability of the metal barrier. The data presented serve as a beginning for needed investigations. Some of the points made in this report are discussed in the following paragraphs.

The authors' summary of general corrosion and oxidation testing for candidate stainless steels states that a conservative corrosion rate of 0.2 um/y can be extrapolated

to show that a 1-cm-thick wall would not be penetrated by general corrosion for over 1000 years. These data are not complete enough in terms of times and temperatures tested to make this assumption. Also, it may not be appropriate to extrapolate one year data at 28°C to 1000 years at repository temperatures since changes in temperatures and the environment could cause the film to thicken and scale off, leaving conditions favorable for the higher corrosion rates exhibited after two months. The tests that ran for one year were conducted at 28°C, and the tests that ran for two months were conducted at 150°C. Experimental weight-loss data in the paper show the corrosion rates to be of 0.242 to 0.285 $\mu\text{m}/\text{y}$ in non-irradiated J-13 water at 28°C after one year and rates of 0.31 to 0.55 $\mu\text{m}/\text{y}$ after two months at 150°C. Corrosion rates based on electrochemical techniques, using Tafel extrapolation and linear polarization in shorter laboratory tests, were stated to be higher but numbers were not given.

It is inappropriate to conclude there are no effects from differences in composition of the austenitic alloys based on weight loss measurements. These compositional effects would be evident using electrochemical measurements.

Stress corrosion cracking (SCC) of austenitic materials occurs intergranularly (IGSCC) in sensitized materials and transgranularly (TGSCC) in chloride environments, and often, failures can have both transgranular and intergranular components. Examples of both SCC failure modes have been observed in AISI 304 used in the cooling system of BWR reactors.

Some studies on pitting, crevice corrosion and TGSCC were reported, and authors of this report indicated stainless steels to be sufficiently resistant to these modes of failure, but indicated that failure could occur under severe environmental conditions. Test data indicated that the stainless steels are not immune to pitting, crevice corrosion or SCC. Anodic polarization data showed hysteresis effects, which indicate a susceptibility to pitting. Additional tests are needed to determine if the protection potential moves in the direction of more negative voltage to make the material more subject to pitting. Alternately wet and dry SCC AISI 304 specimens that were tested for one year showed IGSCC, and some specimens are expected to show TGSCC. TGSCC occurs in more chloride concentrated electrolytes and nonsensitized materials. Conditions in the repository could become severe if ionic concentrations in the water increase due to evaporation.

Gamma radiation caused the corrosion potential to rise for the stainless steel and for both the copper and copper alloys, and removal of the radiation caused the potential to drop. Care in welding and specific welding compositions and parameters for given materials, stainless steel or Alloy 825, are needed. If materials are used in the "as welded" condition, the chemical and mechanical properties and the microstructural stability of the weldments should be investigated to determine the suitability of materials for canister use.

There has been limited testing of copper materials over a two year period, but test results and review information indicate that copper and copper alloys may be feasible candidate materials for use as the waste canister. TGSCC has been found in LM nitrite solutions and nitrite could form from radiolysis of a cupric nitrate surface film on the copper. Studies involving thermodynamic analysis and assuming a stable $\text{Cu}(\text{NO}_3)_2 \cdot \text{Cu}(\text{OH})_2$ film, indicated no change at room temperature due to radiation but other studies identified $\text{Cu}_2(\text{OH})_3\text{NO}_3$ scales. Clarification is needed regarding the composition and structure of the surface film. Anodic polarization tests showed susceptibility to pitting in 0.1 N NaNO_3 at 95°C with pure copper being more resistant than the two alloys. A surface layer of nickel is found under the oxide of one copper alloy and a surface layer of aluminum is found under the oxide of another copper alloy. More data are needed on most aspects of corrosion of copper materials in the tuff repository environment and especially of the effects of oxygen, increased temperatures, radiation and in the area of SCC.

Corrosion test results on carbon steel indicate that a 1-inch-thick liner would last for fifty years. Maximum corrosion rates occur in high oxygen conditions and surface roughening occurs with the widths of selected areas exceeding the depths. More work is needed on this material in terms of effects of oxygen, temperature, pH and irradiation.

RECOMMENDATIONS

More work is needed in most of the major areas discussed in the report, and this need was indicated in the report for a number of cases. Some of the needed work is listed here.

1. Conduct corrosion tests for longer times in simulated repository environments and use electrochemical techniques to obtain data.

2. Conduct studies in the areas of effects of austenitic alloy composition, phase stability and embrittlement on corrosion and durability.
3. Conduct studies of effects of increased concentration of ionic species on pitting, crevice corrosion and stress corrosion cracking.
4. Determine the extent of the effects of gamma radiation of the corrosion and durability of austenitic alloys and copper materials.
5. Determine the structure, composition and stability of the surface film forming on copper materials in the repository environment and relate findings to localized and general corrosion.
6. Conduct corrosion and mechanical property studies on copper materials to show effects of oxygen, increased temperatures and radiation.
7. Conduct tests to determine susceptibility of copper materials to stress corrosion cracking in the repository environment, using methods including slow strain rate tests, U-bend tests, C-ring tests and others as needed.
8. If it is decided to use a borehole liner, galvanic effects and effects of corrosion or degradation products on the remaining waste package materials should be investigated.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues
Already Identified

Related to NNWSI ISTP issues

- 2.2.3 Mechanical failure modes for the waste package container
- 2.2.4 Potential corrosion failure modes for the waste package container
 - 2.2.4.1 Corrosion rates as a function of time
 - 2.2.4.2 Effects of radiation on corrosion failure modes and rates
 - 2.2.4.2.2 Effects of generation of hydrogen, oxygen and other species on corrosion
- 2.3.1 Physical, chemical and mechanical properties of the waste package and how these properties will change with time

(b) New Licensing issues

Effects of sensitization on corrosion behavior of austenitic materials

Effects of welding on microstructures, residual stress levels, chemical homogeneity and ultimately on mechanical integrity, corrosion and hydrogen-induced failures.

Effects of microstructural instability

(c) Comments Relating to Licensing

This report addresses a number of pertinent degradation issues which need to be settled prior to licensing.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

Reed, D. T. and Van Konynenburg, R. A., "Effect of Ionizing Radiation on Moist Air Systems." UCRL-97936, December 1987. Available from NTIS

DATE REVIEWED: 3/17/88, Revised 4/4/88.

PURPOSE

The purpose is to summarize and review the radiation chemistry of the $H_2/O_2/H_2O$ systems.

TYPE OF DATA

Literature review.

MATERIALS/COMPONENTS

None given.

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

None given.

AMOUNT OF DATA

Two Tables

Table I. Partial pressures of Gases after irradiation of N_2/O_2 mixtures.

Table II. Summary of experiments on radiation chemistry of moist air.

UNCERTAINTIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Radiation chemistry, nitrogen, air, nitrogen oxides.

CONCLUSIONS

"There remain a significant number of apparent discrepancies and gaps in the experimental results just reviewed. Some of these discrepancies can be resolved by considering the differences in the experimental conditions of the studies performed. Many of these discrepancies, particularly in the heterogeneous experiments that have been performed, can only be resolved by further experimentation."

GENERAL COMMENTS OF REVIEWER

A fairly comprehensive literature survey, which gives some general indications on the extent of nitric acid formation to be expected under repository conditions. The survey also highlights the need for further experimental work in order to obtain reliable quantitative data on the effects of radiation on the corrosion of the metal containers.

RECOMMENDATIONS

Further experimental work, possibly under conditions more similar to those expected in the repository, is recommended. A radiation chemist could give detailed recommendations on how to proceed.

RELATED HLW REPORTS

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.

APPLICABILITY OF DATA TO LICENSING

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

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

Related to NNWSI ISTP issue, 3.2.1.3, what are the changes in the geochemical conditions of the groundwater due to increased temperature and radiolysis within the saturated/unsaturated zone?

- (b) New Licensing Issues

- (c) General Comments on Licensing

AUTHOR'S ABSTRACT

The radiation chemistry of nitrogen/oxygen/water systems is reviewed. General radiolytic effects in dry nitrogen/oxygen systems are relatively well characterized. Irradiation results in the formation of steady state concentrations of ozone, nitrous oxide and nitrogen dioxide. In closed systems, the concentration observed depends on the total dose, temperature and initial gas composition. Only three studies have been published that focus on the radiation chemistry of nitrogen/oxygen/water homogeneous gas systems. Mixed phase work that is relevant to the gaseous system is also summarized. The presence of water vapor results in the formation of nitric acid and significantly changes the chemistry observed in dry air systems. Mechanistic evidence from the studies reviewed are summarized and discussed in relation to characterizing the gas phase during the containment period of a repository in tuff.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

Van Konynerburg, R. A., Smith, G. F., Culham, M. W., and Smith, H. D., "Carbon-14 in Waste Packages for Spent Fuel in a Tuff Repository," UCRL-94708, October, 1986.

DATE REVIEWED: 7/28/88.

PURPOSE

To review available data in order to assess the behavior of the ^{14}C isotope in a tuff repository environment and whether possible ^{14}C release will be within limits set by the EPA and NRC.

CONTENTS

There is one table in the twelve-page report. Two of these pages list 56 references. The report reviews the following topics in about one page each: (1) the occurrence of ^{14}C naturally, in reactor releases, and health effects, (2) production of ^{14}C in light-water reactors, (3) physical distribution and chemical forms of ^{14}C in spent fuel, (4) the release of ^{14}C from spent fuel in aqueous solutions, in air, in nitrogen, and helium, (5) projected release behavior of ^{14}C from spent fuel waste packages in a tuff repository.

TYPE OF DATA

(1) Scope of the Report

The report is a review and discussion of measurements and calculations of the ^{14}C inventory in spent fuel, the physical distribution and chemical forms of the ^{14}C , and a description of projected ^{14}C behavior in the unsaturated conditions of the tuff repository.

(2) Failure Mode or Phenomenon Studied

The release of the ^{14}C isotope from spent fuel into moist air.

MATERIALS/COMPONENTS

^{14}C isotope; tuff; Zircaloy-clad fuel.

TEST CONDITIONS

(1) State of the Material being Tested

Details of the testing procedures for which the data are summarized are not given.

(2) Specimen Preparation

Details of the testing procedures for which the data are summarized are not given.

(3) Environment of the Material being Tested

The review summarizes data for ^{14}C releases from spent fuel in aqueous solutions, and in air, nitrogen, and helium gases.

METHODS OF DATA COLLECTION/ANALYSIS

Details of the testing procedures for which the data are summarized are not given.

AMOUNT OF DATA

There is one table.

Table 1: "Calculated and Measured Carbon-14 in U. S. Commercial Spent Fuel."

UNCERTAINTIES IN DATA

Not applicable.

DEFICIENCIES/LIMITATIONS IN DATABASE

The deficiencies in the data reviewed are given by the authors in their "Summary and Conclusions" section which is summarized under CONCLUSIONS below.

KEY WORDS

Literature review, air, nitrogen, helium, J-13 water, deionized, Zircaloy, spent fuel (PWR), ^{14}C , ^{14}C release.

CONCLUSIONS

The authors give the following set of conclusions drawn from the review of available data:

1. Published measurements of ^{14}C in U.S. spent fuel are few and deal mostly with Zircaloy-clad fuel (Westinghouse PWR fuel)."
2. In Zircaloy-clad fuel, the uranium oxide contains more ^{14}C than the clad, and the fuel-rod gas contains only a small amount, probably as CO or CH_4 . The chemical form of the isotope in the fuel is not known. The carbon probably exists as interstitial carbon or zirconium carbide in the cladding. [Ed. It is also observed that CO_2 is present inside fuel rods.]
3. A negligible amount of ^{14}C is released from heated, intact spent fuel. This is due to the presence of N_2 , He , which are charged into spent fuel containers to exclude O_2 , which is needed to react with carbon before ^{14}C can be released.
4. On heating an intact PWR fuel assembly, ^{14}C on the external surface was oxidized to CO_2 and released. The isotope may have originated from N in the cladding (precursors to ^{14}C are N , C , and O), or it may have been adsorbed from the reactor cooling water.
5. In less than one year, $>10^{-5}$ of the ^{14}C inventory can be released from spent fuel in aqueous solution.
6. ^{14}C released by pressurized gas escaping when fuel-rod cladding ruptures, may be about 10^{-4} of the calculated total rod inventory. Cladding lifetimes will vary in time.
7. Determination of satisfactory ^{14}C release (the 10CFR60 limit) in an unsaturated tuff repository will depend on the results of measurements of oxidation and release from the spent-fuel rod surface and interior in moist air at temperatures above and below the boiling point of water in the repository.
8. Detailed transport modeling is needed to determine the release limit (according to 40CFR191) for release of ^{14}C from an unsaturated tuff repository. The transport modeling must include factors for dilution of the naturally-occurring carbon which is less abundant relative to the earth's atmosphere.

9. Measurements should be made of the ^{14}C content in (a) the structural components of Westinghouse Zircaloy-clad PWR fuel which do not include Zircaloy, (b) all fuel components from other sources, especially BWR fuel, and (c) fuel clad with stainless steel.

The authors state, "Our current estimates of the ^{14}C inventory are based largely on calculations, which need to be tested against measurements."

GENERAL COMMENTS OF REVIEWER

This report apparently covers the data known at the time of its publication. The authors comment about the need for experimental data, in order to test their calculations, is important. As many specimens of spent fuel as possible should be analyzed to provide accurate inventory estimates in order to understand and estimate the potential for release of ^{14}C from a repository.

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, when, how, and at what rate will radionuclides be released from the waste form.

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory for the
Pacific Northwest Laboratory, Richland, Washington
99352.

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

Westerman, R. E., Pitman, S. G., and Haberman, J. H.,
"Corrosion Testing of Type 304L Stainless Steel in Tuff
Groundwater Environments." UCRL-21005, SANL 616-007,
November 1987.

DATE REVIEWED: 7/26/88

PURPOSE

"The purpose of this study was to evaluate the stress corrosion cracking resistance of solution treated and sensitized 304 and 304L stainless steel at elevated temperatures in tuff rock and tuff groundwater under irradiated and unirradiated conditions by U-bend and slow strain rate tests."

CONTENTS

69 pages: 8 pgs. Title page, table of contents, etc., 4 pgs. Introduction, 2 pgs. Description of Technical Approach, 4 pgs. Materials (3 tables), 5 pgs. Results and Discussion (27 Figures and 9 tables), 2 pgs. Conclusions, 2 pgs. References.

TYPE OF DATA

(1) Scope of the Report: This report covers the results of experiments designed to evaluate 304 and 304L stainless steel as a container alloy.

(2) Failure Mode Studied: Stress Corrosion Cracking, Corrosion

MATERIALS/COMPONENTS

This report focusses on the behavior of 304 and 304L stainless steel. However, samples from the following six different alloys or heats were used for these experiments:

Code No.Material

1	Wrought 304L SS sheet, 1.52 mm thick
2	Wrought 304 SS sheet, 1.52 mm thick
3	Wrought 304L SS plate heat A, 6.35 mm thick
4	Wrought 304L SS plate heat B, 6.35 mm thick
5	Wrought 304 SS plate, 6.35 mm thick and
6	Wrought 316L SS plate, 6.35 mm thick.

The chemical compositions and the mechanical properties of these materials are included in this report as tables 3.1.I and 3.1.II respectively. To distinguish between these materials in this report, the authors use the material code numbers in this review.

TEST CONDITIONS

(1) The State of the Material Being Tested

The alloys were tested in two different conditions of heat treatment: (1) solution annealed and (2) solution annealed and sensitized. The intention was to represent the best and worst possible heat-treatment conditions of the container with respect to intergranular stress corrosion cracking susceptibility. However, various heat treatments were used to achieve these two conditions and the authors do not make a clear presentation of the specific heat treatments used for all samples. The following table is an attempt to assemble heat-treatment information taken from various parts of the report and may be incomplete or contain errors.

<u>Code No.</u>	<u>Solution Anneal</u>	<u>Sensitized Anneal</u>
1	1050°C, 15 m ¹	600°C, 24 h, air cool (ac)
2(a)	1050°C, 15 m ¹	550°C, 24 h, ac
2(b)	1050°C, 15 m ¹	700°C, 24 h, water quench (wq)
2(c)	1050°C, 15 m ¹	700°C, 8 h, wq
3(a) ²	1050°C, 15 m ¹	600°C, 24 h ¹
3(b) ²	1050°C, 15 m, wq	600°C, 10 h ¹
4(a) ²	1050°C, 15 m ¹	600°C, 24 h ¹
4(b) ²	1050°C, 15 m, wq	600°C, 10 h ¹
5	Mill annealed	600°C, 24 h ¹
6(a)	1000°C, 15 m, wq	250°C, 1 day, wq
6(b)	1000°C, 15 m, wq	250°C, 7 days, wq

- Notes: 1. Cooling method not specified.
2. Authors specified 304L but did not specify the heat.

(2) Specimen Preparation

Two different types of samples were used for these experiments. First, U-bend samples were made from the flat sheet materials (Code No. 1 and 2) in the solution annealed and the solution annealed and sensitized conditions. These samples were made by cutting strips 12.7 mm wide and 102 mm long from the 1.5 mm thick sheets and bending them to form a U which is loaded by a bolt. The composition of the bolt, the isolation of the sample from the bolt and the radius of curvature of the bend are not discussed in the report. The U-bend samples were held in place with alumina (Al_2O_3) spacers and rods. The surface treatment, if any, is not specified by the authors. The second type of samples used were tensile samples of square cross section. These samples were cut from the plate materials (Code No. 3-6) and the gage sections of these samples were 25.4 mm long and 6.4 mm wide. The gage sections of these samples were ground (with 220 grit wet/dry paper to remove 0.08 to 0.13 mm) and tested in the as-ground condition.

(3) Environment of the Test

Three different types of tests were used: the irradiation-corrosion test, the boil-down test and the slow-strain-rate test. The environmental conditions used with each of these are described below.

Irradiation Corrosion Tests: For the irradiation-corrosion tests, U-bend specimens were placed into alloy two 600 autoclaves at 50°C and 90°C and exposed to gamma irradiation (^{60}Co) at intensities of 5×10^5 and 3×10^5 rd/h (maximum), respectively. Each autoclave was divided into three zones and duplicate 304 and 304L samples (in the solution-annealed and the solution-annealed-and-sensitized conditions) were mounted horizontally on alumina rods in each zone. The lower zone environment was crushed tuff rock (Topopah Spring tuff rock) and J-13 water. The middle zone environment was crushed tuff rock and air/vapor while the upper zone environment was air/vapor only. The autoclaves were sparged with ≈ 240 ml of air daily to insure the presence of atmospheric gases. The autoclaves were periodically opened and the rock and water replaced after examination of the samples (the rock was not replaced after the 10 months examination). For the 50°C test, these examinations were conducted at 1, 3, 5, 7, 10, 16, and 24 month, and at the test conclusion (25 months). For the 90°C test, these examinations were conducted at 1, 3, 5, 7, 10, and 14 months, and at the conclusion of the test (23 months).

Boildown Tests: For the boildown tests, U-bend specimens were embedded in water-saturated tuff rock fragments and the concentrations of the various dissolved species were increased by periodically boiling off the water present in the autoclave. All of the samples used in these tests were sensitized (heat treatment codes 1 and 2(a-c) above). The autoclave was normally operated at 200°C and 1000 psig, and once every 7 days the back pressure was reduced and the water allowed to boil dry. After 24 h of operation in the "dry" condition, the autoclave was refilled with fresh air-sparged J-13 water. The autoclaves were opened and the samples examined at 3 and 6 months, and testing was halted after 12 months and 50 boildowns.

Slow-Strain Rate Tests: For the slow-strain rate tests, square-cross-section tensile samples were pulled at slow strain rates (1×10^{-4} and 2×10^{-7} m/m-s) in an autoclave environment containing crushed tuff rock through which J-13 well water passed at a slow rate (≈ 35 ml/h) at 95°C and 150°C. The authors refer to an earlier report for a more complete description of this system (Westerman et al. 1982).

METHODS OF DATA COLLECTION AND ANALYSIS

For the irradiation corrosion tests, the autoclaves were periodically opened and the samples examined. Any "obvious" evidence of cracking was considered to be failure and an indication of susceptibility to stress corrosion cracking (SCC). After examining the samples, water samples were taken and analyzed for pH, conductivity and ionic content. Failed samples were examined metallographically. One unfailed specimen from each of the three environmental regions of each of the autoclaves was examined by X-ray photoelectron spectroscopy (XPS) to determine the surface chemistry of this alloy in these environments.

For the boildown tests, the autoclaves were periodically opened and the samples examined. Any "obvious" evidence of cracking was considered to be failure and an indication of susceptibility to SCC. Failed samples were examined metallographically. Water samples were taken under both hot and cold conditions and analyzed for ionic content.

For the slow-strain-rate tests, load and strain were continuously monitored during the test and the fracture surfaces were examined optically, metallographically and in the scanning electron microscope. The reduction in area at fracture, the elongation to fracture, the ultimate tensile strength, the yield strength and the failure mode (ductile, intergranular etc.) were determined for each test. The authors used three indicators to evaluate the relative

susceptibility to SCC. These are: (1) a reduction in the ductility as compared to an inert environment, (2) a diminution of ductility at a particular strain rate as compared to other strain rates and (3) fractographic evidence of a brittle fracture.

To correlate microstructural changes with SCC susceptibility metallurgical examinations and electrochemical experiments were performed on samples after various sensitizing heat treatments. The metallurgical examinations consisted of standard metallography and transmission electron microscopy (TEM). The electrochemical examinations consisted of electrochemical potentiokinetic reactivation (EPRI) measurements. For this technique, the total charge per unit surface area required to repassivate the surface of a sample was measured. Since a sensitized structure will require more charge per unit surface area to repassivate, the magnitude of this measurement is a measure of the sensitization. The exact technique used for these measurements is not discussed in this report.

AMOUNT OF DATA

There are 27 figures and 9 tables.

UNCERTAINTIES IN DATA

The irradiation corrosion experiments at 90°C had a number of operational problems. The autoclave was removed four times from the irradiation access tube and dismantled because of blocking of the air refresh line, and each time the autoclave was opened it was dry due to local overheating and boiling. Repositioning of the control thermocouple corrected this problem, and the tests operated as intended thereafter. This moderate overheating should not alter the metallurgical conditions of the samples so the tests were resumed.

The water analyses showed a great deal of scatter and some relatively high ionic strengths. The solutions showing high ionic strengths of key ingredients were reanalyzed with the results confirming the earlier analyses. This effect was attributed to the "fresh" rock which was added after each examination and so the procedure was altered so that the rock was not replaced when the autoclave was opened for the 10-month and later examinations.

The purpose of the XPS experiments was to evaluate the possibility of surface contamination of the U-bend samples located in the rock/vapor and the vapor only regions of the autoclaves (especially for the 90°C tests). That is, the

authors were concerned that wicking of water with aggressive ions or transport of water droplets during boiling and/or air sparging could be responsible for the high failure rate in the "dry" regions.

In the sixth month of the boildown experiment, the autoclave boiled dry and the temperature rose to 290°C for a 41 h period.

During the sensitization studies, annealing a 304L sample at 600°C for 10 h resulted in a sensitized microstructure while annealing a sample of the same alloy at the same temperature for 24 h resulted in an unsensitized structure. TEM examination showed that a continuous layer of grain boundary precipitate was present in the 10 h sample while no grain boundary precipitates were observed in the sample annealed for 24 h. The authors attributed this result to the fact that the samples used for this study were from different heats (code no. 3 and 4) and that some irregularity in the processing of the steel must be responsible for this difference.

DEFICIENCIES/LIMITATIONS IN DATABASE

The causes and the mechanisms of stress corrosion cracking in the vapor regions of the irradiation corrosion autoclave are unknown. It is likely that the chloride ion caused cracking and that the gamma flux accelerated this process as no SCC of 304L was observed in the absence of gamma irradiation.

The authors concluded that the test conditions differed from the repository conditions because (1) the temperature was not well controlled at the beginning of the 90°C test and boildown occurred, (2) the rock used was surface outcropping containing soluble salts, (3) the method of air sparging might have caused transfer and concentration of chlorides on the specimen surfaces, (4) the gamma irradiation levels were higher than expected in the repository, and (5) the stresses were quite high.

KEY WORDS

Experimental data, corrosion, electrochemical, irradiation-corrosion test, slow-strain-rate test (SSR), spectroscopy, visual examination, U-bend, air plus water vapor, J-13 water, tuff composition, Cl, tuff, cobalt 60, gamma radiation field, ambient pressure, dynamic (flow rate given), high pressure, high temperature, stainless steel, 304 stainless steel, 304L stainless steel, 316L stainless steel, sensitized, solution-treated, slow strain rate, J-13 steam, chloride (low ionic content), corrosion (stress cracking) SCC, cracking, cracking (environmentally assisted).

CONCLUSIONS

- (1) "It was found that solution treated 304L can exhibit transgranular stress corrosion cracking."
- (2) "It is likely that the cracking was chloride induced and accelerated by additional oxidizing power resulting from the gamma irradiation."
- (3) "Most of the failures observed in the gamma flux test occurred in the vapor phase region of the 90°C autoclave" and "test conditions differ from the anticipated repository conditions..."
- (4) "Type 304 stainless steel is more susceptible to stress corrosion cracking than 304L..."
- (5) "When gamma flux was not present, the sensitized 304 exhibited intergranular stress corrosion cracking while the sensitized 304L did not."
- (6) "The 304 stainless steel was found to be susceptible to intergranular SCC in SSR tests performed in 150°C J-13 well water after sensitization at 600°C for 24 h."
- (7) "The susceptibility of 304 SS to SCC in SSR tests was correlated with the formation of grain boundary precipitates. Cracking was intergranular in all cases."
- (8) "Neither 304L nor 316L stainless steel was found to be susceptible to SCC in SSR tests using J-13 well water test environment."

GENERAL COMMENTS OF REVIEWER

(1) Irradiation Corrosion Experiments

General (uniform) corrosion damage was greatest in the rock/vapor and vapor only regions of the autoclave. No obvious evidence of general corrosion was observed on any of the specimens in the rock/water region of the autoclaves. No evidence of pitting was reported by the authors for any of the samples in any of the regions of the autoclaves. A total of 48 U-bend samples were tested (2 alloys, (304 and 304L) x 2 heat treatments (solution treated and sensitized) x 2 replicates x 3 zones in each autoclave x 2 autoclaves) and 15 of these samples failed by stress corrosion cracking (SCC). In the 50°C test, five of the six sensitized 304 samples failed by intergranular SCC. For the 90°C test, 10 of the 24 samples failed by SCC and most of the failures occurred in the

vapor-only region (six). In the vapor-only region, failure occurred in both alloys and heat treatments (sensitized 304 at 3 months and 5 months, solution annealed 304 at 23 months and one no failure, sensitized 304L at 10 months and 14 months and solution annealed 304L at 23 months and one no failure). In this environment, the sensitized 304 failed by intergranular SCC but the other alloy and heat treatments failed by transgranular SCC. In the rock/vapor region of this autoclave, sensitized 304 sample failed by intergranular SCC (at 3 months) and a sensitized 304L sample failed by transgranular SCC (at 14 months). In the rock/groundwater region of this autoclave, both of the sensitized 304 samples failed by intergranular SCC in the first month. No other failures occurred in this region.

It is important to note that these results indicate that neither 304 nor 304L is completely resistant to SCC in the irradiated tuff/groundwater environment of this test. That is, failed samples were produced for each alloy in each heat treatment studied. In fact, one of the two candidate container alloy (304L) samples in its most corrosion resistant condition (solution annealed) failed by transgranular SCC in the vapor only region of this test. While the authors point out five differences between the irradiation corrosion test environment and the expected repository conditions, they do not point out that the environmental conditions of this experiment are closer to the expected environmental conditions of the repository than those of any other experiment reported to date. This reviewer does not feel that the five factors given by these authors are unrepresentative of the repository conditions for the following reasons:

(1) Temperature: The authors reported that the temperature in the experiment was not properly maintained and boildown resulted. The temperature of a waste container in a repository will not be constant and it will vary from point to point on the container. As a result, local boiling may occur and this condition is not unrepresentative of a possible repository condition.

(2) Rock: The authors report that use of fresh outcropping rock resulted in higher concentrations of soluble species than representative of repository conditions. This reviewer does not agree with this point because while the container temperature is above the boiling point, soluble species will concentrate in the rock around the container. Then, when the container temperature drops to the boiling point, water will migrate through these regions redissolving these species. As a result, the first groundwater that

reaches the container will have anomalously high concentrations of soluble species. Therefore, the experimental conditions of this experiment are not unrepresentative of a possible repository condition.

(3) Air-sparging: The method of air sparging might have caused transfer and concentration of chlorides on the specimen surfaces. However, wetting of the container in the repository will not always be uniform and permeation of air thorough the rock to the container should maintain aerated conditions. Therefore, this is not unrepresentative of a possible repository condition.

(4) Irradiation Levels: The irradiation levels were far above those expected for the repository but this was intended to be a severe short-term test. While this is a severe test, it is logical for a conservatively "safe" experiment to use higher than expected radiation levels.

(5) Stress: The applied stresses were well above those expected for the repository. However, this experiment did not evaluate the minimum stress required for SCC, and the extensive secondary cracking or branching shown in the micrographs (e.g. fig. 5.3, 5.5 and 5.6) indicates that mass transport and not stress was limiting propagation. In fact, it appears from the figures that relatively low stresses may be sufficient for crack propagation.

The role of the vapor region is unclear but it is clear that it promoted failure and that it did so by promoting transgranular crack propagation. No transgranular cracking was observed in the 50°C autoclave nor in the rock/groundwater region of the 90°C autoclave. Also, no intergranular SCC was observed on unsensitized samples, but 5 samples failed by transgranular SCC during exposure to air and water vapor at 90°C. Since sensitization promotes intergranular SCC and solution annealing is done to improve resistance to intergranular SCC, one would not expect these heat treatments nor reducing the carbon content to significantly improve resistance to this transgranular failure process and indeed both solution annealed and sensitized samples of 304L failed by transgranular SCC. It appears that there may be two different mechanisms of SCC occurring in these samples. The first is intergranular SCC of sensitized 304. This probably proceeds by stress assisted preferential dissolution of the material in the chromium depleted regions adjacent to the grain boundaries. It is unclear how this process can proceed in the absence of an aqueous phase unless water droplet transport or condensation occurred but 5 of the 6 sensitized 304 samples in each autoclave (50°C and 90°C) failed by

intergranular SCC. The second SCC mechanism was that observed in the vapor containing regions of the 90°C autoclave which resulted in transgranular failure. The mechanism and important factors contributing to this type of failure in this environment are unknown and the results reported by these authors are preliminary. Clearly, more research is needed so that we can understand how this type of environment can cause transgranular SCC of solution annealed 304L and so we can avoid failure of 304L, or any other container material, by this process.

(2) Boil-down Tests

All ten of the 304 U-bend samples used in this test failed while none of the 304L samples failed. These results appear contradictory to those reported above unless gamma irradiation is required by the transgranular SCC mechanism. However, the boil-down tests were run for only 12 months and 50 boil-downs. Failure by transgranular SCC was not observed until the 10 month inspection and all of the transgranular SCC failure occurred in regions which were nominally dry for the entire 10 to 23 months. For the boil-down tests, the autoclaves were dry for only one day a week and testing was halted with only 50 days of "dry" operation. Since 50 days is considerably less than 10 months, the results of the boil-down tests do not contradict the results of the irradiation corrosion tests nor do they indicate that gamma irradiation is required. Also, the concentrations of salts at the base of a dried out water droplet will be greater than those in an autoclave which is refilled with J13 water after even 50 boil-downs.

(3) Slow-Strain-Rate Experiments

The sensitized 304 samples exhibited intergranular SCC while no SCC was observed for the other alloys and heat treatments. While these results may seem contradictory to the irradiation corrosion test results unless gamma irradiation is required for transgranular SCC, that is not really the case. First, the samples were completely immersed in J13 water and no vapor phase was present. Second, no attempt was made to concentrate the solution. Since all of the transgranular SCC failures occurred in the vapor regions of the autoclave and no transgranular SCC failures were observed in the regions where the samples were in contact with J13 water, one would not expect the same type of failure to occur in these tests.

(4) Sensitization Studies

The sensitization study is rather preliminary. The TEM diffraction conditions are not given for the micrographs and the reviewer cannot evaluate the micrographs from xerographic

copies. The authors attribute the observed difference in the sensitization behavior of the 304 to precipitate morphology and for the 304L to chemical differences in the samples. Further studies will be required to verify these assumptions.

RELATED HLW REPORTS

Westerman, R. E., Pitman, S. G., and Nelson, J. L., "General Corrosion, Irradiation-Corrosion, and Environmental-Mechanical Evaluation of Nuclear Waste Package Structural Barrier Materials," PNL-4364, Pacific Northwest Laboratory, Richland, Washington, 1982.

APPLICABILITY OF DATA TO LICENSING

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

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

This report relates to NNWSI ISTP issue 2.2.4, the potential failure modes for the waste package container form dissolution mechanisms.

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

Aines, R. D., "Application of EQ3/6 to Modeling of Nuclear Waste Glass Behavior in a Tuff Repository," UCID-20395, May, 1986. Available from NTIS.

DATE REVIEWED: 10/8/87. Revised 2/2/88.

TYPE OF DATA

Preliminary development of glass degradation modeling capabilities for repository performance assessment modeling, using the geochemical modeling code EQ3/6.

MATERIALS/COMPONENTS

None given.

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

Development of computer geochemical code.

AMOUNT OF DATA

3 Tables

1. Species and hydration reactions of the hypothetical oxide and silicate components of glass (Grambow, 1984)
2. Phases reported to form on nuclear waste glass.
3. Additional precipitates on nuclear waste glass.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Computer program, planned work, geological modeling code, defense high level waste (DHLW).

CONCLUSIONS

"Modeling of glass degradation based on sound geochemical principles appears to be possible with revisions to EQ3/6. Realistic source terms for several repository scenarios may be generated with such a model. One scenario which appears very likely and which is also amenable to modeling using EQ3/6 is that in which an intact but perforated canister holds water in contact with waste glass. The water overflows continuously or periodically, allowing radionuclides to come in contact with repository rocks. This isolated-type scenario will be the first realistic modeling effort because it limits complex interactions between rock and glass. However, EQ3/6 modeling should be possible even for very complicated scenarios if sufficient experimental data are available on rates and thermodynamics. This will be the limiting factor in progress toward modeling the complete system."

GENERAL COMMENTS OF REVIEWER

EQ3/6 is a geochemical modeling code which can be used for repository performance assessment modeling. This report describes preliminary development of glass degradation modeling capabilities using this code. The authors believe that our current understanding of glass leaching mechanisms and the interaction of glass with an aqueous environment has advanced to the point where it is now feasible to begin designing models for long-term behavior of waste glass under repository conditions. The report outlines the principles to be used in design such a model. A staged development is outlined that would take a number of years to complete. Milestones of this staged development are listed in the report and at each stage the modeling effort would be verified with experimental work.

Because the model is only in its initial planning stage, sufficient detail is given to judge the validity of the final product in assessing radionuclide release under realistic repository conditions. Even when completed and checked against experiment, it is difficult to see how the model could be sufficiently comprehensive and accurate to

predict exactly the performance of the waste package. However, when the final model is checked against experiment, it could probably be used to predict the effects of changes in various parameters. Judgment of the effectiveness of the model for long-term performance prediction must at the least await its experimental verification in the short-term.

More specific comments are given below regarding the author's plan to adopt the EQ3/6 method in assessing the long-term performance of waste form.

(1) The author does not provide us with any directions on how we can modify the existing models of chemical reactions in the EQ3/6 in the additional presence of waste-glass components, which is, the reviewer believes, the key to the proposed work by the author. The presence of metastable glass components or radiation field may make the existing methods inappropriate because of their metastability and of the unknown radiation effects. Concomitantly, this may lead to invalidate the numerical methods developed in the EQ3/6.

(2) The author is recommended to propose some ways to estimate these new interactions among glass components, radiation field and geological environment. The reviewer believes that he does not have to wait for the complete experimental data, which may be practically impossible. There might be indirect ways to prove any proposed models. For instance, the thermodynamic model of glass dissolution used the free energy of hydration as an indirect or even empirical parameter and the results have turned out to be very useful.

(3) Short-term kinetics do not appear to be an important issue to be considered in the proposed work by the author, since the time frame under consideration is very long compared with that for diffusion-limited or non-congruent dissolution.

APPLICABILITY OF DATA TO LICENSING

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

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

This report relates to NNWSI ISTP issue 2.3.2.1.2, the rates of dissolution associated with the potential waste form dissolution mechanisms.

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

Aines, R. D., "Plan for Glass Waste Form Testing for NNWSI," UCID-21190, September 1987. Available from NTIS.

DATE REVIEWED: 5/23/88; Rev. 6/28/88.

PURPOSE

The purpose of the glass waste form testing plan is to provide accurate data and models concerning glass leaching in the repository and to ascertain that there is adequate information to assess the importance of all release mechanisms.

TYPE OF DATA

- (1) Collection and integration of existing glass waste form information.
- (2) New glass waste form leach data to determine overall degradation rates, radionuclide release rates, solution compositions in contact with glass and mechanism of degradation.
- (3) Glass release modeling using existing glass waste form information and computer code EQ3/6.

MATERIALS/COMPONENTS

Glasses identified in the producer's Waste Compliance Plans and Waste Qualification Reports will be tested. These presently include West Valley Demonstration Project (WVDP) and Defense Waste Processing Facility (DWPF) glasses. Other components will include materials likely to be found in the repository such as stainless steel and tuff.

TEST CONDITIONS

Parametric studies based on the unsaturated test and static leaching methods will be made. The unsaturated test method will be based on that developed by Bates and co-workers while the static methods will be based on MCC-1 and the pulsed flow method developed at the Vitreous State Laboratory, Catholic University of America.

Tests will be conducted at 90°C with J-13 water previously equilibrated with tuff rock at the test temperature. Some data will be obtained at 60°C to determine temperature dependence of the leach rates and some data will be obtained using deionized water for comparison with data currently available. Testing will be conducted on both simulated and radioactive samples of glass from both producers (Savannah River Plant (SRP) and WVDP).

METHODS OF DATA COLLECTION/ANALYSIS

These subjects are not addressed in this document but may be found in the related High Level Waste (HLW) documents cited below. These documents are included in the data base.

CONTENTS

29 pages; 1 figure cited below; purpose and objectives, 3 pgs; rationale for selected studies and quality assurance 3 pgs; description of tests and analysis, and previous work, 9 pgs; glass release modeling 3 pgs; application of results 1 pg; schedule and milestones, 3 pgs; list of test plans to support this study plan, 1 pg; references 2 pgs.

AMOUNT OF DATA

1. Glass Waste Form Testing Information Flow.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Planned work, leaching, EQ3/6, laboratory, J-13 water, deionized, tuff composition, tuff, basic (alkaline)

solution (pH >7), high temperature, glass (West Valley reference glass), glass (defense waste reference glass), matrix dissolution (glass).

CONCLUSIONS

There are no conclusions.

GENERAL COMMENTS OF REVIEWER

The basic organization of the plan is excellent. The functions described in the plan will be carried out by many organizations so that careful and diligent overview of the effort will be required.

Three main efforts in the plan are compilation and selection of existing data for preliminary modeling tests, obtaining new leaching data on waste glasses supplied by SRP and WVDP, and development of a long-range modeling program based on the EQ3/6 program.

The author states that elucidation of the glass leaching mechanism is paramount to the success of the modeling effort. The leach mechanism may be extremely difficult if not impossible to define so that validation of a geochemical model is a formidable challenge.

The coupling of kinetic and thermodynamic modeling in the EQ3/6 model needs to be subjected to much thought. The basic assumption appears to be that glass will be leached by a kinetic process and that leach components will crystallize out on the glass surface by a thermodynamic process. However, in this coupled process either the thermodynamic or kinetic process could be rate controlling. For example, crystallization of SiO_2 in the form of a complex silicate will decrease the concentration of dissolved silica in the reaction zone and may lead to an increased leach rate.

Many reports have dealt with the formation of crystalline deposits on leached glass surfaces. An often unstated assumption concerning this phenomena is that the crystalline deposit protects the glass from further leaching. Because of the coupled kinetic leaching and thermodynamic recrystallization equilibria, leach rates could actually increase rather than decrease due to this effect. An important data need is the fate of radioactive nuclides in the host glass. The fraction of radionuclides captured in the recrystallized glass needs to be known.

RELATED HLW REPORTS

Bates, J. K., and T. Gerding (1985). One-Year Results of the NNWSI Unsaturated Test Procedure: SRL-165 Glass Application, ANL-85-41, Argonne National Laboratory, Argonne, IL.

Mendel, J. E. (compiler) (1984). Final Report of the Defense High-Level Leaching Mechanisms Program, PNL-5157, Ch. 1, Pacific Northwest Laboratories, Richland, WA.

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 concerning when, how, and at what rate will radionuclides be released from the waste form.

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

E.I. duPont de Nemours & Co., Savannah River
Laboratory, Aiken, South Carolina 29808.

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

Boersma, M. D., "Process Technology for Vitrification
of Defense High-Level Waste at the Savannah River
Plant," DP-MS-83-135. Paper prepared for proceedings
of the American Nuclear Society Meeting, Fuel
Reprocessing and Waste Management, Jackson Hole,
Wyoming. August 26-29, 1984. Available from NTIS.

DATE REVIEWED: 8/17/87; Revised 4/4/88.

TYPE OF DATA

(1) Scope of the Report:

The descriptive paper presents a process overview, a review
of the characteristics of the high-level radioactive waste
to be processed, descriptions of unit process operations,
and process parameters used to vitrify high-level
radioactive waste.

(2) Failure Mode or Phenomenon Studied:

Description of DWPF high-level radwaste vitrification
process.

MATERIALS/COMPONENTS

Detailed in paper are high-level, liquid sludge and slurry
radioactive waste forms and volumes, chemical compositions
of the radwaste sludge and salts resulting from initial
waste treatment, and calculated inventories of wastes on a
"design basis" (Table IV).

TEST CONDITIONS

(1) State of the Material being Tested:

Physical, chemical, and radiological characteristics of
anticipated alkaline liquid sludge, saltcake, and saturated

salt solution waste are detailed for the Savannah River Plant (SRP).

(2) Specimen Preparation:

Processing of SRP waste to remove salts, precipitates, and sludge is described. Decontamination procedures of the bulk of the salt solution for disposal as low-level chemical waste disposal are detailed. Concentration processing of the remaining radionuclides for vitrification is also described, as are preparation of intermediate process by-products.

(3) Environment of the Material being Tested:

Radwaste processing conducted mainly in a liquid and radioactive environment. Salt separation and solids pretreatment uses specially-designed equipment within existing, sealed waste tanks outside the DWPF building. Decontaminated salt solutions will be blended with Portland cement in a separate facility for earthen trench subsurface burial. Radionuclide separation and processing will occur in the DWPF building. Radwaste sludge will be further processed within the DWPF building to adjust physical slurry properties, and to remove gases and mercury compounds to prepare slurry feed stock for vitrification. Vitrification, canister filling, and canister decontamination will also be carried out within the DWPF.

METHODS OF DATA COLLECTION/ANALYSIS

Parameters shaping the scope of the radwaste disposal program are based both on existing calculated radwaste inventories and DWPF goal to reduce inventories in next 10-15 years. Composition of material to be processed and vitrified in that time period is based on anticipated "design basis" of radionuclide inventory.

AMOUNT OF DATA

Figures

1. Defense High-Level Waste Treatment at the Savannah River Plant (process flow chart)
2. Sludge Receipt and Adjustment Tank (cutaway schematic)
3. DWPF Melter (cutaway schematic)
4. Off-Gas Film Cooler with Brush Reamer (cutaway schematic)
5. Welding Process (cutaway schematic)

Tables

- I. SRP High Level Waste Volume, lists Column 1 - volumes (cubic meters) of sludge, salt cake, and salt solution in current inventory and Column 2 - respective rates of increase (cubic meters per year).
- II. Chemical Ingredients of SRP Waste Sludge (Dry Basis), Column 1 - 12 sludge ingredients, Column 2 - as received weight percentage range, and Column 3 - expected DWPF feed range weight percentage.
- III. Composition of SRP Salt Waste, Column 1 - 12 SRP salt waste compounds, and Column 2 - weight percentage of each on a dry basis.
- IV. Aged SRP Waste Radionuclides, Column 1 - 22 isotopes in aged SRP waste, Column 2 - half-life in years, Column 3 - Ci/L in 5 year old sludge, Column 4 - mg/L of 5 year old sludge, Column 5 - Ci/L of 15 year old supernate, and Column 6 - mg/L of 15 year old supernate.
- V. Typical DWPF Glass Frit, lists column 1 - 5 frit compounds, and Column 2 - weight percentage of each.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Design, simulated field, Savannah River Plant, air, ambient temperature, basic solution, defense high level waste (DHLW), vitrification, borosilicate glass, high-level radioactive waste, low-power alkaline waste, glass melting, off-gas treatment, slurry, sludge, salt solution, frit, melter, stainless steel canister, canister decontamination, upset resistance weld.

GENERAL COMMENTS OF REVIEWER

This paper is a good, detailed overview of the vitrification processing of defense high-level waste at the Savannah River Plant. 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 data (X)

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

Related to ISTP issue 2.3.2, concerning 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

E. I. duPont de Nemours and Company, Savannah River Plant, Aiken, South Carolina 29808.

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

Boersma, M. D. and Mahoney, J. L., "Glass Making Technology for High Level Nuclear Waste." Paper proposed for presentation at the American Institute of Chemical Engineers Meeting, Boston, MA, DP-MS-86-75, August 24-27, 1986.

DATE REVIEWED: 8/17/87; Revised 4/2/88.

TYPE OF DATA

(1) Scope of the Report:

Descriptive paper discusses principles and design of an air-tight DWPF melter and associated unit processes in detail. Unit operations of batching, melting, and forming involved in the DWPF are discussed, with emphasis (in decreasing order of priority) on batching and melting.

(2) Failure Mode or Phenomenon Studied:

Wet batch processing and production of vitrified nuclear waste materials is described with particular emphasis on details and advantages of wet vs. dry batch processing and melting.

MATERIALS/COMPONENTS

Materials described are high-level nuclear waste sludge is treated to yield soluble nonradioactive salts, soluble radioactive species, mercury, gases, and high-level radioactive metal hydroxide sludge precipitates. Radioactive waste materials are combined with glass frit for melting and nuclide immobilization.

TEST CONDITIONS

(1) State of the Material being Tested:

Sludge precipitates containing nonradioactive salts and radioactive metal hydroxide precipitates.

(2) Specimen Preparation:

Soluble, nonradioactive salts are separated from sludge and disposed of in solid low-level waste forms. The remaining raffinate sludge is further processed for incorporation in vitrified borosilicate glass waste forms. Glass matrix formed from carefully sized, premelted, crushed or ground frit mixed with treated sludge. Melting combines slurried glass matrix frit with slurried high level waste sludge. Gaseous melting byproducts and melting particulates are concentrated in the off-gas system and recirculated back through the melting process or filtered and discharged to the atmosphere following dilution.

(3) Environment of the Material being Tested:

Sludge resulting from neutralization is stored in an aqueous environment in selected DWPF steel underground liquid waste-storage tanks. Immobilizing glass is melted in a special air-tight melter in the DWPF facility. The melter is designed to channel off-gases either back into melting process or to post-melting treatment, incinerate residual waste stream organics, pyrolyze nonvolatile organics in waste stream and other melting remnants. Molten glass package is poured into and contained within metal canisters in DWPF for long-term repository storage.

METHODS OF DATA COLLECTION/ANALYSIS

Prior testing of melter models and research scale melters used to accumulate operating and design data for present operational DWPF melter - (see present article reference 5.), K. R. Routt, "Modeling Principles Applied to the Simulation of a Joule-Heated Glass Melter", DP-1540, E. I. duPont, Savannah River Laboratory, 1980.

AMOUNT OF DATA

Figures

1. DWPF Slurry Processor (cutaway schematic)
2. Steam Stripping Efficiency vs. Mercury Concentration
y-axis Water/Mercury Mass Boilup Ratio, 250 - 4250
(linear)
x-axis Hg Concentration in Sludge, Wt% Dry Basis, 0 - 2.4% (linear)
3. DWPF Melter Feed System (cutaway schematic)
4. Mercury Displacement Pump (schematic)
5. DWPF Melter (cutaway schematic)

6. Riser and Pour Spout Heaters, Conceptual Cutaway View
(cutaway schematic)

UNCERTAINTIES IN DATA

Uncertainties in existing data and performance parameters will, in the words of the authors on pages 15-16 of the reviewed report, "provide challenges to chemical engineers for years to come as performance is optimized and design improvements are made in replacement melters".

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Radioactive waste fixation, vitrification, glass melter, wet slurry batching, slurry feeding, borosilicate glass frit, fused-cast chrome-alumina refractory.

CONCLUSIONS

This report addresses specific and unique chemical engineering aspects of the Defense Waste Processing Facility at the Savannah River Plant. Besides conventional three unit operations: batching, melting and forming, nuclear waste vitrification also requires a major sidestream process, off-gas decontamination. While the forming is a trivial process, the rest three operations are based on unique concepts with various rationales. To obtain (1) good quality assurance in products and processes, (2) safe operation and safe storage, and (3) simple packaging, various chemical adjustments and new process devices are used. More details of these concepts are described in the section entitled GENERAL COMMENTS OF REVIEWER. The developed process is very efficient for most compounds with typically >95% yield of waste solids ending up in the glass.

GENERAL COMMENTS OF REVIEWER

Concepts in article detailed and well thought-out. Rationale for various unit operations within overall immobilization process consistent with good glass melting practice. Operating details draw on existing waste disposal and glass technology, or rely on data and operational practices derived from modeling and pilot scale studies.

Unit Operation: Forming

Concept: Merely pouring the molten glass from the melt into a large mold with uncontrolled natural cooling.
Rationale: Trivial step in nuclear waste glass.

Unit Operation: Batching

Concept: Unusual dilute aqueous solutions and slurries.
Rationale: Superior quality assurance in chemical accuracy, homogeneity and sampling. No radioactive dust.

Concept: Chemical Adjustment: removal of nonradioactive salt and leaching of sludge solid.
Rationale: To reduce inert volume, to remove troublesome species and to improve melter performance.

Concept: Glass formers: particle size, angularity, melting behavior, direct cost are controlling factors.
Rationale: To simplify storage and delivery systems, and minimize batching errors.

Concept: Pumping: feeding of the melter at two points and special desing (figure 3).
Rationale: To ensure good distribution on the melter surface, and to be radiation resistant, reasonably long-lived and remotely replaceable.

Unit Operation: Melting

Concept: High Density, fused-cast, chrome alumina refractory liner.
Rationale: To prevent the attack of metals and refractories by the molten glass.

Concept: Plenum Heater
Rationale: To achieve the glass production rates desired and to ensure combustion of vitrification gases to burn organics.

Concept: Silicon controlled rectifiers for temperature control.
Rationale: To eliminate the potential for sending a DC current rather than an AC current through the melt.

Concept: Replaceable thermowell.
Rationale: Not to allow the current flow to the grounded melter shell.

Concept: Type B thermocouple.
Rationale: For the long-term resistance to drift or failure at elevated temperatures.

Concept: TV camera.
Rationale: Direct determination of the amount of feed pile coverage to prevent the unwanted pressure surges.

Concept: Water system.
Rationale: To provide passageways that carry the molten glass from the main chamber and discharge it into the product canister.

Concept: Motive System.
Rationale: Starting and stopping glass flow from the melt into the product canister.

Unit Operation: Off-gas treatment

Concept: Film cooler
Rationale: To prevent glass deposits from sticking to the walls of the exit pipe.

Concept: Injected gas: the line at above dew point of water, HCl, H₂SO₄ and etc.
Rationale: To cool the bulk off-gas for the condensation of some salts.

Concept: Jet Ejector.
Rationale: To remove most of large entrainment particles from the off-gas.

Concept: Knock-out system.
Rationale: To reduce cesium concentration and to avoid frequent change-out of filters.

Concept: Collapsing wake steam jet atomized scrubber, pipe upstream of a centrifugal separator, and other atomized scrubbers and filters.

APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues 2.7.2, how will the waste package design ensure that the radioactive wastes will be in solid form in a sealed container and 2.7.3, how will the waste package design ensure that particulate waste forms will be consolidated (for example, by incorporation into an encapsulating matrix) to limit the availability and generation of particulates?

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

E.I. du Pont de Nemours & Co., Savannah River Laboratory,
Aiken, South Carolina 29808.

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

Daugherty, B. A., Salizzoni, L. M., and Mentrup, S. J.,
"Processing of Transuranic Waste at the Savannah River
Plant," paper proposed for presentation at the Waste
Management '87 meeting, Tucson, AZ, DP-MS-86-48, March
1987.

DATE REVIEWED: 8/17/87; Revised 3/30/88.

TYPE OF DATA

(1) Scope of the Report:

General background and review of the design of the transuranic (TRU) waste processing facility (TRWF) at the Savannah River Plant.

(2) Failure Mode or Phenomenon Studied:

TRU waste processing and immobilization.

MATERIALS/COMPONENTS

Transuranic waste containing both combustible and non-combustible materials in sludge and resin form contained within 55-gallon drums and carbon steel boxes.

TEST CONDITIONS

(1) State of the Material being Tested:

Transuranic waste containing both combustible and non-combustible materials in solid, sludge and resin form.

(2) Specimen Preparation:

(3) Environment of the Material being Tested:

Air, earthen burial, waste preparation area (WPA), deep geological repository.

METHODS OF DATA COLLECTION/ANALYSIS

General design information.

AMOUNT OF DATA

Figures

1. The Process Flow, (schematic)
2. Waste Preparation Cell, (schematic)

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Design, Savannah River Plant, field, air, earth, ambient temperature, ambient pressure, transuranic waste (TRU), Waste Isolation Pilot Plant (WIPP), deep geological repository, TRU Waste Facility (TWF), remote operation, hydrogen explosion, sand filters, high-efficiency particulate air (HEPA) filters, verification, solidification, Waste Certification Facility (WCF).

GENERAL COMMENTS OF REVIEWER

Good general overview of transuranic waste facility (TRWF) planned for the Savannah River Plant.

APPLICABILITY OF DATA TO LICENSING

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

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

Related to ISTP issues 2.7.2, how will the waste package design ensure that the radioactive wastes will be in solid form in a sealed container?, 2.7.3, how will the waste package design ensure that particulate waste forms will be consolidated (for example, by incorporating into an encapsulating matrix) to limit the availability and generation of particulates?

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

AUTHOR'S ABSTRACT

The Department of Energy (DOE) has instituted a national program to isolate defense TRU waste in a deep geological repository, the Waste Isolation Pilot Plant (WIPP), in Calsbad, New Mexico. Since 1972, the highly toxic and long half-life transuranic (TRU) waste at the Savannah River Plant (SRP) has been stored on above-grade concrete pads in 55-gallon drums, large carbon steel boxes, and concrete culverts. As part of the national program, a major project is planned at SRP to retrieve and process this waste. This project, the TRU Waste Facility (TWF), will provide equipment and processes to retrieve TRU waste from 20-year retrievable storage and prepare it for permanent disposal at the WIPP. This project is an integral part of the SRP Long Range TRU Waste Management Program to reduce the amount of TRU waste stored at SRP. The TWF is designed to process 15,000 cubic feet of retrieved waste and 6,200 cubic feet of newly generated waste each year of operation. This facility is designed to minimize direct personnel contact with the waste using state-of-the-art, remotely operated equipment. In support of the TWF, a remote size-reduction and material handling process is being cold-tested at the Savannah River Laboratory. The process consists of a large, low-speed shredder and material handling system, a remote worktable, bagless transfer system, and a robotically controlled manipulator.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

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

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

Eisenstatt, L. R., Chapman, C. C., and Bogart, R. L., "A Method for Showing Compliance with High-Level Waste Acceptance Specifications," Waste Management '86, Proceedings of Symposium on Waste Management, Tucson, AZ, March 1986, R. G. Post, editor, Volume 2, pgs. 513-519, 1986.

DATE REVIEWED: 5/12/87; Revised 9/23/87; 4/20/88.

TYPE OF DATA

(1) Scope of the Report:

Analysis.

(2) Failure Mode or Phenomenon Studied:

Methods, including process analysis, that the WVDP will be using to construct the waste form, and to show that the waste form will meet the preliminary specification of DOE.

MATERIALS/COMPONENTS

WV-205, Defense Waste Reference Glass (DWRG), Stainless steel ASTM A240, UNS Designation S30400/ Canister, Purex C-Sampler.

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

None given.

AMOUNT OF DATA

Tables

1. Composition of WV-205 (the standard glass that was recently selected.)

2. Variations on WV-205 that will be studied for radionuclide release rate.

Figures

1. West Valley vitrification flow diagram. Feed sample locations during nonradioactive process model testing are designated (in the flow sheet.)
2. West Valley glass variability approach. (The acceptable glass area and the test boundary are shown within a triangular diagram.)
3. Purex C-Sampler. (The sampling system that is now being tested.)
4. Leach rates versus residence time results from the partial exchange interactive flow test for WV-205 and DWRG glasses. The normalized leach rate and the annual fractional loss per year is shown. Time scale: 0.001 - 1 (y), Leach rate: $10^{-3} - 1$ ($\text{g}\cdot\text{m}^{-2}\text{d}^{-1}$).
5. West Valley canister. (Schematic of the preliminary design for the West valley canister is shown.)
6. West Valley canister grapple. (Conceptual design of the grapple being tested at West Valley is shown.)

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Planned work, process analysis, stainless steel, defense high-level waste (DHLW), West Valley, vitrification, canister, sampling.

GENERAL COMMENTS OF REVIEWER

This paper deals with the approaches that will be used by the West Valley Demonstration Project (WVDP) to show that the West Valley HLW glass waste form product will meet the preliminary specifications of D.O.E. for waste disposal.

The glass that will be generated will be characterized for chemical composition, crystallinity, and radionuclide release. During the process the characteristics of the glass will be monitored by measurements of the viscosity and conductivity at the melting temperature. Initial testing will take place with nonradioactive simulated waste glass. The WVDP will attempt to prove that it is not necessary to sample the radioactive end-product (i.e., the actual waste glass) and that the composition of the product can be obtained from sampling the Concentration Feed Makeup Tank (CFMUT).

The most important issue in deciding whether such testing is acceptable is the degree of homogenization of the sludge in the melter. One of the important parameters in our understanding of the homogenization process is the Residence Time Distribution (RTD) in the melter. This function 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⁽¹⁾

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

RELATED HLW REPORTS

1. Wolf, D. and White, D., "Experimental Study of the Residence Time Distribution in Plasticizing Screw Extruder," AIChE Journal 22, 122-131, (1976).

APPLICABILITY OF DATA TO LICENSING

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

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

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

- (b) New Licensing Issues

- (c) General Comments

AUTHOR'S ABSTRACT

The West Valley Demonstration Project is in the process of showing that the West Valley high-level waste product will be acceptable for disposal. The methods that are being considered emphasize testing nonradioactive components and relating them to the radioactive production product. Glass and canisters processed at the Component Test Stand at West Valley will be studied to provide the basis for showing that the tested components are similar to those that will be produced during production. This testing will include defining and testing glass compositions that may be generated, process model development and verification, and canister design and testing. Administrative controls will

need to be instituted to ensure that restricted materials are not included in the canistered waste form and to ensure that the proper materials are procured. During production accurate records will need to be kept.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

E.I. du Pont de Nemours & Co., Savannah River Laboratory,
Aiken, South Carolina 29808.

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

Maher, R., Shafranek, L. F., and Stevens, W. R.,
"Solidification of Savannah River Plant High-Level
Waste," paper presented to a meeting of the American
Institute of Chemical Engineers, Washington, DC,
DP-MS-83-110, November 1983.

DATE REVIEWED: 8/17/87; Revised 3/30/88.

TYPE OF DATA

(1) Scope of the Report:

Review paper describing technology and engineering to "convert the 30 million gallons of sludge, salt, and liquid presently in the waste tanks into approximately 1 million gallons of glass" in a vitrification operation.

(2) Failure Mode or Phenomenon Studied:

High-level defense waste immobilization.

MATERIALS/COMPONENTS

Defense radioactive waste materials, borosilicate glass waste immobilization form, stainless steel containment canisters.

TEST CONDITIONS

(1) State of the Material being Tested:

High-level defense waste radionuclide materials, present as metal oxide and salts, present as a liquid sludge.

(2) Specimen Preparation:

Radwaste will be physically and chemically treated to separate various nuclide forms and fractions, then combined either with cementitious materials or with glass forming frit and melted for immobilization.

(3) Environment of the Material being Tested:

Sludge is stored in a sealed liquid radioactive environment. Processing will take place within the sludge containment environment. Further sludge processing, melting, canister filling, and canister decontamination will occur in the DWPF facility. Long-term canister storage will be in deep mine repositories.

METHODS OF DATA COLLECTION/ANALYSIS

Data in paper is of a general design nature, collected from referenced sources.

AMOUNT OF DATA

Twenty one figures listed, consisting of process flow charts, process materials, or photographs of DWPF facilities or equipment:

- Figure 1. Source of Radioactive Wastes at Savannah River, (flow chart)
- Figure 2. Radioactive Liquid Waste, (photographs)
- Figure 3. Actual Waste Sludge, (photograph)
- Figure 4. Salt in Waste Tank, (photograph)
- Figure 5. New Waste Storage Tank, (cutaway schematic)
- Figure 6. Waste Tank Farm, (aerial photograph)
- Figure 7. Defense Waste Processing Facility, (flow chart)
- Figure 8. Shielded Cells, (photograph)
- Figure 9. Large Slurry-Fed Melter, (photographs)
- Figure 10. Inside Sludge Removal Demonstration Tank Before Sludge Removed, (photograph)
- Figure 11. Inside Sludge Removal Demonstration Tank Most Sludge Removed, (photograph)
- Figure 12. Inside Sludge Removal Demonstration Tank After Sludge Removal, (photograph)
- Figure 13. Glass Waste Canister, (photograph)
- Figure 14. Defense Waste Processing Facility, (artists drawing)
- Figure 15. DWPF Building 221-s - Level 1, (schematic)
- Figure 16. DWPF Melter Off-Gas System, (photograph)
- Figure 17. Off-Gas Line Cooler, (photograph)
- Figure 18. DWPF Building 221-S - Section C, (schematic)
- Figure 19. Interim Storage Building, (artists drawing)
- Figure 20. Glass Storage Building Section B - B, (schematic)
- Figure 21. Saltstone Monolith Cross Section, (schematic)

UNCERTAINTIES IN DATA

Only general process design data presented.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Process design, facility design, Savannah River Plant, air, ambient temperature, ambient pressure, basic (alkaline) solution, stainless steel, defense high level waste (DHLW), solidification, high-level waste, waste form, sludge, slurry, salt, liquid, saltcake, waste tank, borosilicate glass, DWPF, repository, joule heating, stainless steel canister, off-gas, decontamination.

GENERAL COMMENTS OF REVIEWER

Paper presents general overview of DWPF history, design, development, and operations.

APPLICABILITY OF DATA TO LICENSING

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

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

Related to ISTP issues 2.7.2, how will the waste package design ensure that the radioactive wastes will be in solid form in a sealed container?, 2.7.3, how will the waste package design ensure that particulate waste forms will be consolidated (for example, by incorporating into an encapsulating matrix) to limit the availability and generation of particulates?

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Report

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

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

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

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

TYPE OF DATA

(1) Scope of the Report

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

(2) Failure Mode or Phenomenon Studied

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

MATERIALS/COMPONENTS

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

TEST CONDITIONS

(1) State of the Material being Tested

Glass monoliths and powders.

(2) Specimen Preparation

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

(3) Environment of the Material being Tested

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

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

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

METHODS OF DATA COLLECTION/ANALYSIS

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

AMOUNT OF DATA

There are seven tables.

Table 2.1--"Comparison of Calculated Elemental Leach Depths, from Solution and Gel Layer (EDXS) Concentration Data, with Those Observed by SEM/EDXS in a DWRG Alteration Region Produced in 183 Days of IAEA-76 Type Testing in

Deionized Water at 90°C." Calculated Layer Thickness and SEM/EDXS-Based Layer Thickness, both in microns, are given for nine elements.

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

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

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

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

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

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

There are 34 figures.

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

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

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

Figure 2.4--"Three SEM Micrographs of the 30-Micron-Thick Alteration Zone Formed on a 360-Grit-Polished DWRG Sample in 183 Days of Water Exchange Testing at Catholic University. conditions: deionized water, 25% volume water exchange at intervals from 1 to 30 days, 90°C, SA/V = 7 m⁻¹." The micrographs show Outer Surface at 300x, Edge View at 1000x, and Inner Surface at 300x.

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

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

Figure 2.7--"SEM Micrographs Showing Pitting of the DWRG Beneath the Alteration Layer, Produced During Static Leaching Under Various Conditions." Four micrographs are shown all at 200x magnification: Deionized Water, 28 days, 3 micron polish; Deionized Water, 28 days, 600 grit polish; Deionized Water, 143 days; Deionized Water + Canister Metal, 7 days.

Figure 2.8--"SEM Micrographs Demonstrating the Effects of precipitate Deposition on the Extent of Pitting of the DWRG Surface During Leaching. conditions: 7 days MCC-1

leaching at 90°C in deionized water with an equal surface area of the reference canister metal and DWRG." Four micrographs are given: Top Surface of DWRG at 2000x; Bottom Surface of DWRG at 2000x; Top Leached Glass Surface at 200x; Bottom Leached Glass Surface at 200x.

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

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

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

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

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

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

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

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

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

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

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

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

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

Figure 2.23--"SEM Micrographs and EDXS Spectrum of a Weeksite-Type $[\text{Na}_2(\text{UO}_2)(\text{Si}_2\text{O}_5)_3 \cdot \text{H}_2\text{O}]$ Uranium-Containing Crystalline Phase formed in Both silicate and Deionized Water Leaching of the DWRG and TDS-131."

Figure 2.24--"SEM Micrographs and EDXS Spectrum of a Tobermorite-Type Product $[\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 8\text{H}_2\text{O}]$ Formed in Leaching of the DWRG and TDS-131 Glasses at 90°C at High SA/V."

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

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

Figure 2.27--"SEM Micrograph, EDXS Spectrum, and XRD Pattern of the Mixed Magnesium Oxychloride $[\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O} - \text{Mg}_{10}(\text{OH})_{16}\text{Cl}_2 \cdot \text{H}_2\text{O}]$ Preferentially Formed on the Surface of the DWRG in MCC-1 Static Leaching in Brine at 90°C for 28 Days."

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

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

Figure 2.30--"EDXS Trace and SEM Micrographs of Weeksite Clusters. Left, tapered weeksite crystals over an analcime crystal, calcium silicate sphere (see Figure 2.34) to top right, run 3-C (201°C, 158 h). Right, (run 20-F, 230°C, 1800 h) bluntly terminated blades of weeksite; in the background are analcime, calcium silicate (Figure 2.31) and two forms of silica. (See Figure 2.34 right top and bottom). Scale bars 100 microns."

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

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

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

Figure 2.34--"EDXS Trace and SEM Micrographs of "Silica" Phases. Stout prisms (left): this morphology resembles that of quartz (SiO₂) although DCP/AES analysis shows the presence of Li and B in addition to Si, run 20-C (230°C, 1800 h). Laths (bottom right): the individual crystals resemble those figured by Savage (1981), although the organization in the cluster is different (run 20-F, 230°C, 1800 h). Ragged cluster (top right): sphere in background is calcium silicate (see Figure 2.33 A), run 21-D (225°C, 361 h). Scale bars 25 microns."

UNCERTAINTIES IN DATA

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

DEFICIENCIES/LIMITATION IN DATABASE

None given.

KEY WORDS

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

GENERAL COMMENTS OF REVIEWER

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

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

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

The presence of reactive solids such as canister metal or ductile iron in the leach system with initially air-saturated deionized water, significantly accelerates the removal of silica from the glass and leads to the formation of colloidal complexes and well-defined crystalline precipitates on the surface. Small node-like and flocculent precipitates are common in all systems where water flow is low enough for saturation to occur. This may indicate that crystallization on the altered layer is occurring. However, in deoxygenated deionized water the reaction is much less aggressive which indicates the importance of the Eh in this case.

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

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

APPLICABILITY OF DATA TO LICENSING

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

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

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

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

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

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

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

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

TYPE OF DATA

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

MATERIALS/COMPONENTS

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

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

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

AMOUNT OF DATA

Tables

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

Figures

- 5.1 Expected volume changes as a function of dose and correlated to the waste storage times of both defense and commercial high-level waste forms. Dose range: 10²¹-10²⁷ alpha decays/m³, swelling range: (-1)-(+6)%.
- 5.2 Increase in relative leaching L/L₀ versus volume change, for percent volume change from 0 to 40% and increasing leaching factor from 0 to 80.
- 5.3 Total gas pressures generated by salt solutions in a ⁶⁰Co irradiation field. Normalized dose range: 0-25 Grd, pressure range: 0-100 atm.

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

UNCERTAINTIES IN DATA

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

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Literature review, brine, basalt composition, granite composition, tuff composition, salt, Cl, Br⁻, SO_4^{2-} , basalt, granite, tuff, alpha radiation field, gamma radiation field, redox condition, commercial high level waste (CHLW), defense high level waste (DHLW), ^{239}Pu , groundwater, corrosion (general), leaching (radiation enhancement), radiation effects.

GENERAL COMMENTS OF REVIEWER

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

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

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

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

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

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

APPLICABILITY OF DATA TO LICENSING

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

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

Related to ISTEP issues, 2.2.4.2, concerning the effects of radiation on the corrosion failure modes and associated corrosion rates for the waste package

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

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Work performed under the auspices of the U. S. Department of Energy by the Westinghouse Hanford Company, Richland, Washington under Contract No. W-7405-Eng-48.

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

Smith, D. H., "The Influence of Copper on Zircaloy Spent Fuel Cladding Degradation Under a Potential Tuff Repository Condition," UCRL-15993, SANL 622024, Lawrence Livermore National Laboratory, March 1987. Available from NTIS.

DATE REVIEWED: 2/7/88.

TYPE OF DATA

Experimental.

MATERIALS/COMPONENTS

Materials Characterization Center's Approved Testing Material, ATM-101 spent fuel rods were wrapped in copper foil of 99.999 wt. percent purity to make a bundle and placed in a 0.1M $\text{Cu}(\text{NO}_3)_2$ solution in a fused silica jar with a Pyrex lid. Some areas of spent fuel rods were polished to permit observation of a newly formed oxide film.

TEST CONDITIONS

Each bundle contained approximately 400 g of spent fuel, and the gamma radiation dose rate at the bundle surface was about 1000 Rd/h. The $\text{Cu}(\text{NO}_3)_2$ solution was held at a temperature of 90°C, and the solution pH was approximately 4.5. Tests were conducted for periods of two and five months. Lost liquid due to sampling was replaced with an equal amount of stock solution. Solution lost due to evaporation was replaced with an equal volume of deionized water.

METHODS OF DATA COLLECTION/ANALYSIS

Inductively coupled plasma optical emission spectroscopic analysis was used to detect Zr. Specimens were photographed at the end of the test. X-Ray diffraction was used to identify $\text{Cu}_2(\text{OH})_2\text{NO}_3$ deposits and the partially oxidized copper wrap. Specimens were sectioned for microscopic observation. Metallographic techniques were used to view the cladding with the original oxide and cross sections showing the metal/oxide interface. Electron probe analysis, with a profile line sensitivity of 0.1 % of 1 %, was conducted on the oxide film cross section, and no Cu was detected. Scanning electron Microscopy (SEM) was used to evaluate polished and unpolished areas of the specimens and also the oxide/ metal interface. Energy dispersive x-ray analysis (EDX) showed the presence of Fe and Si but Cu was found in only one of eighteen specimens studied. Auger electron spectroscopy was coupled with ion milling to produce elemental concentration profiles through the oxide film and into the Zircaloy as a function of time. The observation of copper was considered as a contaminant on the surface.

AMOUNT OF DATA

There are two tables and six figures.

Tables

Table I. A Comparison of Some Expected Tuff Repository Environmental Conditions with Those in Which Copper has been Observed to have Influenced Zircaloy Corrosion.

Table II. Average Observed Ion Milling Time to Achieve a 90% Decrease in Surface Oxygen Concentration and an Equivalent Increase in Surface Zirconium Concentration.

Figures

1. Schematic of Corrosion Cell Used for the 2-Month and 5-Month Experiments. Copper foil wrap with a copper wire tie holds the bundle together. Zircaloy plugs are press fit to mechanically seal each cladding section.
2. Before and After Photographs of the Cladding Bundle Used in the 2-Month Experiment. Discontinuity in texture of deposits about half way up on the copper wrap indicates the water level during the experiment. Note that the polished cladding is still shiny after two months.

3. Sectioning Diagram for Each Ring Specimen (see figure 2). Ring segments were evaluated via SEM, Auger/ion milling, electron microprobe and metallography.
4. Example of Thick Films on H. B. Robinson Spent fuel Cladding From the 5-Month Experiment.
5. Scanning Electron Micrographs of Cladding Samples With Thin Oxide From the 2-Month Experiment: a) Total specimen with well defined boundary between polished (right) and unpolished (left) areas, b) High magnification SEM micrograph of boundary showing oxide (dark) and metal (light) areas. Notice that the oxide-metal interfact shows no topographical expression.
6. Auger Electron Spectrum for Specimen P2 from the 2-Month Experiment, Copper, sodium, and calcium seem to be present on the undisturbed surface and are quickly removed by sputtering, i.e., the surface after 30 seconds of sputtering (Post-sputter surface) doesn't show these elements. All 12 specimens from 2- and 5-month experiments exhibited very similar spectra.

UNCERTAINTIES IN DATA

Calculated oxide film thicknesses on the Zircaloy were 115 Å after two months and 145 Å after five months. Experimental values were similar to these but the scatter in the data was greater than the difference in the thickness values.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Experimental data, supporting data, microscopy, spectroscopy, surface film, x-ray diffraction, laboratory test, Yucca Mountain, 0.1 M $\text{Cu}(\text{NO}_3)_2$ solution, Cu, acidic solution, 90°C temperature, copper, spent fuel(BWR), Zircaloy, spent fuel cladding, degradation, oxidation, corrosion.

GENERAL COMMENTS OF REVIEWER

These tests were conducted to investigate whether copper ions accelerate zirconium alloy corrosion in acid environments and whether crud induced local corrosion (CILC) would occur in a repository environment. Neither accelerated corrosion nor crud-induced localized corrosion were observed after these tests. The testing conditions used are not representative of those in the repository or of the conditions under which

accelerated corrosion and crud-induced localized corrosion would occur. Nodular corrosion, the precursor to CILC in Zircaloy was produced by other workers at a temperature of 510°C and a pressure of 1500 psig, and it would not have been expected under conditions of the testing described in this report. Additional tests designed to accelerate local corrosion of Zircaloy should be conducted before conclusions are made regarding effects of copper on Zircaloy's corrosion behavior in the repository environment.

APPLICABILITY OF DATA TO LICENSING

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

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

This report relates to NNWSI ISTP issue, 2.3.6, regarding potential damage and failure mechanisms for the fuel rod cladding.

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

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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

Wilson, C. N., Einziger, R. E., Woodley, R. E., and Oversby, V. M., "LWR Spent Fuel Characteristics Relevant to Performance as a Wasteform in a Potential Tuff Repository", UCRL-92891, June 1985. Available from NTIS.

DATE REVIEWED: 12/14/87; Revised 3/2/88.

TYPE OF DATA

Literature review of leach studies from PWR spent fuels and oxidation of spent fuel.

MATERIALS/COMPONENTS

None given.

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

None given.

AMOUNT OF DATA

None given.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Literature review, spent fuel leaching, laboratory, air, J-13 water, deionized, high temperature, basic (alkaline) solution (pH >7), neutral solution (pH = 7), spent fuel, spent fuel oxidation, ^{237}Np , ^{238}Pu .

GENERAL COMMENTS OF REVIEWER

This report is essentially a review of the related HLW reports cited below which have been previously reviewed and are included in the NBS data bank. In addition, new observations, not described, state that examination of partially oxidized spent fuel particles and ion microprobe data on spent fuel, which was partially oxidized using $^{18}\text{O}_2$, support previous data suggesting grain boundary oxidation as the initial stage in the oxidation process. No data are given.

RELATED HLW REPORTS

Wilson, C. N., and Oversby, V. M., "Radionuclide Release from PWR Fuels in a Reference Tuff Repository Groundwater," UCRL-91464, March 1985.

Einzigler, R. E., and Woodley, R. E., "Low Temperature Spent Fuel Oxidation Under Tuff Repository Conditions," HEDL-SA-327iFP, 1985.

APPLICABILITY OF DATA TO LICENSING:

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

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

Report relates to NNWSI 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

Appendix C. The NIST Comments on the Yucca Mountain CDSCP

Appendix C

The NIST Comments on the Yucca Mountain CDSCP

Section 7.4.5.6 Corrosion Model

Comment

Corrosion models should be specific and/or be adaptable to given metals, environmental conditions, and forms of corrosion.

Basis

- The electrode potential of a metal or a phase within an alloy and the repository environment will control initiation or absence of corrosion. Electrode potentials should be known for varying conditions and times of exposure.
- Changes in water chemistry such as pH and/or ionic content will affect the electrode potential of the exposed metal.
- Surface film formation on a given metal as related to composition, electrode potential and corrosion rate must be established.
- Localized stresses, brittle phases, precipitates, different phases and other microstructural variations will result in variations in electrode potential and corrosion processes.
- Corrosion processes expected should be correlated with the material and environment.

Recommendations

- Use standard testing methods to determine and verify corrosion behavior of candidate repository materials in repository environments.
- Measure electrode potentials associated with given corrosion reactions in the repository environment.
- Set up corrosion data base for each material, environment, temperature and condition.
- Set up corrosion data base for previously determined corrosion data that will be used as a basis for projecting corrosion rates or behavior. (Note: There is a lot of scatter in some corrosion data, and this must be dealt with for modeling or predicting.)

Section 8.3.4.2.1.3 Composition of Vadose Water from the Waste Package Environment

Comment

Evaporation of vadose water will be responsible for salt transport to the canister area during the period in which the temperature exceeds about 95°C. The composition of vadose water may differ from the reference J-13 groundwater.

Basis

- Corrosion of the canister and dissolution of the waste form may be strongly dependent on groundwater chemistry.

Recommendations

- Theoretical models for comparison of vadose water composition should be described.
- Criteria indicating "contaminated water" should be explained.
- Plans for characterization of corrosivity of the vadose water in relation to the candidate canister material must be made.

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

Comment

There is no description of the development and use of standardized test methods which have undergone peer review.

Basis

- These test methods are needed for determining the stability and durability of the nuclear waste and the waste package materials.
- The tests must be acceptable in terms of reliability and reproducibility.

Recommendations

- Make use of the Materials Characterization Center (MCC), which was established by the DOE in 1980, to ensure that qualified materials data are available on nuclear waste and waste package materials. Meeting this goal must include development of acceptable standardized test methods.
- Use MCC test method development and approval procedures as a first step in obtaining acceptable compliance data.
- The site characterization plan should contain a section describing test method development and test method approval, and data reliability, precision and accuracy.

Section 8.3.5.9.1.1.2 Microstructural Characterization

Comment

Metallographic and microscopic characterization techniques given in this section for copper, copper-based alloys, and austenitic stainless steels are inadequate.

Basis

- Chemical etchants are selected to show a specific feature of a microstructure, but may not show other critical characteristics.
- Some microstructures cannot be observed using conventional metallographic techniques.
- Grain boundary structure, precipitate formation, and dislocation structures affect material properties and stability, and these features should be viewed at high magnifications of transmission electron microscopy.
- Chemical analysis, x-ray analysis, hardness measurements and other techniques would be needed to analyze for oxygen, hydrogen, or other elemental diffusion into metals.

Recommendations

- Establish standard procedures for studying microstructures of materials being considered for use in nuclear waste storage.
- Establish necessary specific methods for characterizing microstructures of a given material.
- Methods should be specified for the material and microstructural considerations in question.

Section 8.3.5.9.1.1.2 Phase stability in austenitic stainless steels

Comment

Microstructures of austenitic stainless steels are unstable in terms of transformation to martensite, precipitation of sigma or other embrittling phases and sensitization, and data are not available to show effects of prolonged exposure to 100 to 400°C temperatures expected in the repository.

Basis

- Small amounts of martensite increase the steel's susceptibility to stress corrosion cracking.
- Embrittling phases provide initiation sites for cracking and increase susceptibility to cracking.
- Sensitization or carbide formation may be enhanced by initial high temperatures and by extended elevated temperatures of the repository. Beneficial effects of carbide forming alloying elements such as titanium and of specified cooling rates during manufacture could be negated by the extended time at temperature after emplacement.
- Phase precipitation causes chemical changes in the microstructure which will result in decreased resistance to localized corrosion such as pitting and stress corrosion cracking.

Recommendations

- The microstructure and associated properties should be established to be stable in given repository conditions before selecting the material for use in the repository. Any metastability should be characterized and demonstrated to not adversely affect predicted performance.
- Data should be collected under simulated repository conditions to show microstructural changes which will and will not occur.
- Effects on sensitization of alloy composition and time at repository temperatures should be studied.

Section 8.3.5.9.1.1.4 Subactivity 1.4.11.4. State of Stress in the Container

Comment

The analyses of the state of stress at various locations should include analyses of fabrication and handling flaws which will not be detected by non-destructive evaluation (NDE) and inspection procedures.

Basis

- This section states that changes in the state of stress with time and temperature will be evaluated at a number of locations, but it does not specifically state that fabrication and handling flaws are considered in these analysis.
- Pores, inclusions, stringers, etc. can occur during fabrication of the container and the presence of these can alter the stress state.
- Mishandling of the container can result in alterations in the residual stress pattern and the size and shape of surface flaws.

Recommendations

- The evaluation should take into account fabrication and handling flaws, and should identify limiting flaw sizes for different geometries.
- The limiting flaw sizes and geometries should then be used as design parameters for the development of fabrication procedures and the establishment of non-destructive testing techniques and practices to be used at the site.

Section 8.3.5.9.1.1.4 Subactivity 1.4.11.4. State of Stress in the Container

Comment

The plan should take into account temporal changes in the state of stress due to corrosion of the container.

Basis

- This section states that changes in the state of stress with time and temperature will be evaluated at a number of locations, but it does not specifically state that corrosion damage is included in this evaluation.
- Wall thinning due to corrosion processes will alter the stress state.
- If localized corrosion (pitting, crevice corrosion, etc.) occurs, it will result in the formation and growth of flaws which act as stress concentrators.

Recommendations

- Analysis of the state of stress at various locations in the container and changes in the state of stress with time should account for the influence of corrosion as well as temperature.
- Corrosion processes can alter the geometry of the wall by reducing the wall thickness and by promoting the formation and growth of stress concentrating flaws.
- The probability of formation of stress concentrating flaws and the expected rate of growth of these flaws should be accounted for in the analyses.

Section 8.3.5.9.1.1.5 Weld Inspection

Comment

Metallurgical characterization of prototype welds should be made to characterize microstructures and chemistry and to determinate their effects on weld integrity.

Basis

- Welds are areas of chemical inhomogeneity, and effects of this inhomogeneity under repository conditions should be established.
- Welds of austenitic stainless steels are areas subject to sensitization that may lead to failure.
- Weld solidification shrinkage can result in localized increases in stress that can promote stress corrosion cracking and other cracking.
- Weldments have the potential for contamination and local segregation, either of which may promote premature failure.
- Welded areas are potential sites for galvanic corrosion and localized corrosion.

Recommendations

- Establish, for each material considered for repository storage, the metallurgical and microstructural properties which result after welding.
- Conduct studies, of the metallurgical aspects of weldments, that involve exposure of weldments to simulated repository conditions.
- Evaluate data in terms of long term stability and durability.
- Conduct tests to determine effects of welded microstructures and weldment chemistry on corrosion behavior.
- Effects of composition, welding conditions and repository environment should be established.

Section 8.3.5.9.2.2.1 Assessment of Degradation Modes
Affecting Candidate Copper-Based Container Materials

Comment

The scientific basis for degradation modes of copper-base alloys in the CDSCP is not in agreement with scientific literature. This causes concern that future plans may be improperly drawn.

Basis

- Only T-SCC (transgranular stress corrosion cracking) is being considered. However, I-SCC (intergranular SCC) is known to occur for many copper-base alloys, in particular α -brass in the presence of an oxide film, in aqueous NH_3 solutions.
- The role of NH_3 in the electrolyte is assumed to be that of dissolving a protective film. However, T-SCC in pure copper, for instance, requires the presence of a film.
- Since T-SCC in some copper-base alloys has been observed in conditions where copper was not being dissolved, the existence for critical electrical potentials for SCC prevention seems rather doubtful.
- There is no convincing evidence that selective leaching (dealloying) occurs exclusively through a dissolution-precipitation mechanism

Recommendations

- The section (p. 59-79) should be rewritten so as to reflect a better understanding of the scientific literature.

Section 8.3.5.9.2.2 Degradation Modes Affecting Candidate
Copper-Based Container Materials

Comment

There is no indication of the reasons for choosing three specific copper-base alloys as candidate container materials.

Basis

- 3 materials CDA 102, CDA 613, and CDA 715 are going to be tested
- Other copper-based alloys could perform as well or better than the three listed.
- Except for these 3 materials, no tests, not even scoping tests, have been performed on other potential, or candidate copper-base alloys.

Recommendations

- A program for preliminary testing of other copper-base alloys should be initiated, and
- A more detailed and convincing argument should be made to justify the selection of certain copper-base alloys as candidate materials.

Section 8.3.5.9.2.3.2 Subactivities 1.4.2.3.2. -
1.4.2.3.9. Laboratory Test Plan for Austenitic Materials

Comment

The experimental approach for each possible degradation mode should be designed and evaluated prior to testing. How will "more severe" environments be identified and proven to be "more severe" for a given failure mode?

Basis

- The design of an experiment can determine the outcome. Therefore, it is important that each experiment be thoroughly evaluated as to its appropriateness to test a possible failure mode or to yield information for use in a given model.
- Various investigators will disagree as to the value of experimental designs, and their differences need to be considered and then resolved or accommodated.
- The relative severities of environments can be difficult to evaluate and quantify. Proving that a given environment is "more severe" may become difficult.

Recommendations

- A procedure should be established to evaluate the appropriateness, so as to establish whether it can be used in (1) evaluation of a possible failure mode, or (2) providing information to be used in a model.

Section 8.3.5.9.2.3.2 Subactivities 1.4.2.3.2. -
1.4.2.3.9. Laboratory Test Plan for Austenitic Materials

Comment

The possibility that the container may come into contact with dissimilar metals is not addressed in this section.

Basis

- The container may come into contact with various alloys in the repository (spacers and bare plates, etc.) or with the fuel rods inside the container.

Recommendations

- The possibility of galvanic coupling should be identified as an area of concern.
- Potential couples and procedures to avoid galvanic coupling should be identified.
- Where galvanic coupling cannot be avoided, experimental and modeling programs should be established to address this possibility and the expected results of the various conceivable couplings.

Section 8.3.5.9.2.3.2 Subactivities 1.4.2.3.2. -
1.4.2.3.9. Laboratory Test Plan for Austenitic Materials

Comment

The effects, on the corrosion behavior of the containers, that may result from any metallurgical changes associated with fabrication in large sections is not identified as a specific topic of a test program.

Basis

- Metallurgical conditions associated with large sections can differ considerably from those of small laboratory samples. As a result, the corrosion behavior can be considerably different.
- The size of the section and the welding procedures govern metallurgical conditions and, thus, they alter the corrosion behavior.
- Other fabrication processes and procedures (such as shot peening [1]) may alter the surface and metallurgical condition of the container and thereby alter the corrosion behavior of the container.

Recommendations

- The impact of fabrication procedures on the corrosion behavior of full size containers should be evaluated.

References

- CDSCP Section 8.3.5.9.1.1.4 State of Stress in the Container

Section 8.3.5.9.3.2.1 Subactivities 1.4.3.2.1
Metallurgical Aging and Phase Transformations

Comment

The resistance of an alloy to corrosion, intergranular corrosion, and stress-corrosion cracking is a function of the combined effects of radiation, temperature, stress, and time on the metallurgical stability of the alloy

Basis

- Changes in the metallurgical condition of austenitic materials can have dramatic effects on the resistance of these materials to degradation by chemical as well as mechanical processes.

Recommendations

- This section should address the effect of metastability of austenitic materials on the resistance of these materials to degradation by chemical (corrosion), and combined chemical and mechanical (stress-corrosion) processes, as well as purely mechanical processes.

Section 8.3.5.10 Corrosion of Zircaloy

Comment

Corrosion of Zircaloy depends on the repository environment, composition and metallurgical condition, and the previous history in service and storage.

Basis

- The type of reactor exposure, the composition of the residue that collects on the fuel rods, and the manner in which the fuel rods were cleaned will affect corrosion of Zircaloy.
- Residue deposits that contain copper have especially destructive effects on Zircaloy's protective oxide film, and local corrosion or pitting may result.
- Zircaloy, in reactor service, is subject to stress corrosion cracking from the fuel side of the cladding due to fission products such as iodides.
- Liquid metal embrittlement has been reported for Zircaloy in contact with molten cesium, liquid sodium or cadmium.
- Examples of hydrogen embrittlement failures in Zircaloy cladding have been reported.
- Zircaloy is not immune to pitting corrosion and pitting can occur in hydrochloric acid which contains ferric or cupric ions and in the presence of all the halogens either in liquid or gaseous form.

Recommendations

- Conduct corrosion studies to measure electrode potentials for Zircaloy in the repository environment, and to determine effects of varying temperature, ions present, water and oxygen.
- Use standardized tests to determine the susceptibility of Zircaloy to stress corrosion cracking in the repository environment.
- Study structural formation of the oxide film, and determine effects of wetting, drying and other conditions of the repository.

- Use standard tests to determine susceptibility to hydrogen embrittlement and cracking.
- Conduct standard tests to determine pitting susceptibility of Zircaloy.
- Study effects of welding on the corrosion behavior of Zircaloy.

Section 8.3.5.10 Issue Resolution Strategy for Issue 1.5.
Will the Waste Package and Repository Engineered Barrier
Systems Meet the Performance Objective for Radionuclide
Release Rates as Required by 10 CFR 60.113?

Comment

The leaching of spent fuel may be an important factor in meeting the performance objective for radionuclide release.

Basis

- The solubility or leachability of spent fuel will be enhanced if it is oxidized in the repository environment.

Recommendations

- Define an alternate strategy for prediction of spent fuel oxidation and dissolution.

Appendix D. MCC--Materials Characterization Center

Appendix D

MCC -- Materials Characterization Center

A. Program Administration

The MCC Program Manager met with DOE officials in Washington, DC in January to discuss the MCC FY 1988 Technical Program Plan, and in February, J. C. Haugen, Materials Integration Office, discussed revisions to the FY 1988 Technical Program Plan with members of the MCC. A new Hardware Sampling Task, sponsored by the Systems Integration Program at PNL, was authorized for the MCC. This new task is aimed at acquiring and characterizing activated metals, such as materials used in the disassembly of spent fuel and in associated bearing reactor components. The MCC should locate and evaluate sources of hardware samples and determine what analytical facilities and procedures are needed and whether these facilities are in place or need to be added to conduct hardware analyses under NQA-1/PNL MA-60 Level 1 conditions. The MCC contacted thirty-five electrical utilities, and got generally favorable response. Three types of non-fuel bearing reactor components (NFBC) will be obtained. These are (1) a cruciform control rod (CCR) that has been in service in a General Electric Boiling Water Reactor (BWR), (2) a burnable poison rod assembly (BPRA) and (3) a full-length rod cluster control assembly (RCCA) that has been in service in a Westinghouse Pressurized Water Reactor (PWR). The cost of acquiring these components will be in the range of \$159K to \$179K. If suitable cask liners are not available and have to be acquired, there will be an additional \$50K to \$100K cost. Reactor components of particular interest are those which were exposed in the low-flux regions at or near the ends of the fuel assemblies. All analytical procedures necessary to determine compositions of irradiated components are approved or in process. The actual materials acquisition for this task is proposed for FY 1989. Hardware from assemblies of ATMs-103, -104, -105 and from subsequent ATMs will be analyzed.

B. Quality Assurance.

Corrective actions were taken pertaining to the West Valley audit EA-87-5 and were acknowledged as complete by West Valley. Minor problems relating to test material related activities were corrected. Audit EA-8801 was performed and a draft report given on February 26, 1988. Three concerns were identified for the MCC were technical aspects of spent fuel operation procedures, conflicts between the Nuclear

Waste Handbook, PNL-3990 and MCC technical procedures and lack of evidence that an independent technical review of the ORIGEN2/VAX software requirements form was completed.

Five surveillance reports, KSW-88-004-A, -005-A, -007-A, -008-A and -009-A were completed. It was reported that the Commission of European Communities (CEC) leach tests were conducted in compliance with the test procedure. Both static and flow-through tests are included in the "CEC Repository Simulation Testing Round Robin". West Valley leach tests were conducted according to procedure MCC-TP-5, Rev. 2 and Test Instruction MCC-TP-5-TR-7, fission gas sampling per MCC-TP-10 was properly documented, pulsed flow leachate data were well managed and there was verification for compliance with MCC-TP-8 and fuel rod identification and argon purging of a storage container. Surveillance reports, KSW-88-010-A, -006-A and -012-A regarding repackaging of spent fuel samples, macrophotography of spent fuel specimens and performance of length measurements of three impact test canisters, respectively, were completed. The Statement of Work (SOW) for the post-irradiation testing laboratory (PITL) had to be changed since PITL was not able to do some photography and Boeing Computer Services Richland (BCSR) was requested to do the work.

A surveillance, KSW-88-003-A, resulted in a deficiency report involving the ceramography and metallography of spent fuel specimens, and problems were identified with document control, calibration, laboratory record books and data reporting.

FY 87 impact test records and samples of test materials were sent to Sandia National Laboratories. The final Basalt Waste Isolation Project record turnover was completed. The final Salt Repository Project records were transferred in June, 1988, closing out the MCC portion of this project. ATM-10 fabrication records, requested by Lawrence Livermore National Laboratory, were turned over to them.

One new staff member was trained in the MCC project scope, organization and QA plan.

West Valley advised that their MCC work should be performed at PNL Quality Level 2. A memo was written describing Quality Levels 1 and 2. It was requested that Quality Level 3 be applied to the Comprehensive Data Base.

C. Support to the Office of Geologic Repositories, through April, 1988 - New name as of May, 1988 is Support to the Office of Siting and Development

a. Waste Glass Round Robin

The MCC Waste Glass Analytical Round Robin Workshop was held in February 9-10, 1988 in Chicago, Illinois with nineteen participants from seven different laboratories and the MCC. Laboratories represented included Vitreous State Laboratory, Catholic University of America, Ames Laboratory, Iowa State University, Lawrence Livermore National Laboratory, Westinghouse Hanford Company, Savannah River Laboratory, West Valley Nuclear Services and Pacific Northwest Laboratory. Results of the analytical round robin completed in October, 1987 are given in Table 1 (reference, MCC April, 1988 monthly report). These results show that most participants analyzed the glass samples successfully but some individual laboratories had single element discrepancies. Figure 1 (reference, MCC April, 1988 monthly report) shows a comparison of round robin duplicate specimens, 1 and 2, for the different laboratories. Preparation of sample solutions, for inductively coupled plasma (ICP) instruments, continues to be a concern in achieving analytical accuracy and precision. ICP-MS (mass spectroscopy) methods appear to be the principal procedures for determining elements in low concentration. Preparations have begun for the next round robin in the continuing series conducted by the MCC among nuclear waste glass producers and repository developers.

b. Spent Fuel Operations

Spent fuel rods are gamma scanned and this data is accepted, and then fission gas sampled. Four ATM-105 (BWR) fuel rods were retrieved and gamma scanned. Two of the four have been fission gas sampled and segmented. The ATM-104 fuel rod to be characterized this year was gamma scanned and is ready for fission gas sampling. The remaining inventory of ATM-106 rods were gamma scanned and fission gas sampled, and a rod that has a high fission gas release, (1475 cm³ of fission gas), was selected for characterization in FY 88. An ATM-106 rod was fission gas sampled, and there were no indications of any gas present. This result had occurred once before with a BWR rod. This same result occurred with two out of twelve rods, and it is disconcerting since less than 1 percent of all fuel rods have been predicted to have leaks. Revision of the gamma scanning system software has been completed and MCC-TP-9 was revised. MCC-TP-10 for fission gas sampling was revised.

There was a QA audit concern, regarding the fact that no maximum time limit was set for exposure of cut rod exposure to air before being placed in an inert atmosphere. This question was reviewed and indications were that fuel oxidation would not be as much a concern as fission product reaction. Other individuals will be consulted regarding recommended time limits for limiting fission product exposure to air. Following this QA audit, specimens of ATM-106 which were sectioned for tests and archiving, were inserted into sample containers or vials which were filled with argon.

Measurements of ^{14}C in the fuel, cladding, crud and gas are being made and evaluated. It was determined that earlier measurements of ^{14}C were reasonable taking into account the uncertainty in the value for the nitrogen content (Activation of ^{14}N produces ^{14}C). Some measurements of the nitrogen content in the fuel and cladding will be made in the future to check the variation in the measured and assumed values.

Analytical transmission electron microscopy (AEM) is being conducted on fuel-rod specimens. Gas bubble (xenon) and five-metal-particle pairs are observed. The five metals are molybdenum, ruthenium, technetium, palladium and rhodium. Some ceramographic and metallographic results show that migration of fission products is consistent with release of fission gas. Gamma scans indicate that some ATM-106 rods have extensive cesium migration and a moderate to high fission gas is expected.

Proximity sensors used in measuring fuel rod length sometimes fail, due to radiation damage of the wire. Alternative methods of measurement which are accurate to 1/4 inch, should be acceptable when failure of proximity sensor occurs.

A meeting was held and it was agreed that spent-fuel characteristics and ATM selection criteria will appear in a revised PNL-4686, "LWR Spent Fuel Approved Testing Materials for Radionuclide Release Studies" to be issued by the MCC.

Several other areas which fall under Support to the Office of Geologic Repositories are included in this paragraph. A new fuel-rod storage container was fabricated and installed. The ATM-103 characterization report was reviewed, approved by DOE-RL, printed and distributed. Work continues on grain boundary gap inventory and assay methods. A draft report on ATM-105 BWR fuel was completed and sent off site for comments. A draft of procedures for

shipping spent-fuel ATM samples to Oak Ridge National Laboratory (ORNL) for spark source mass spectrometric analyses was received for review, and a set of samples from fuel rod 104-MKP-109 was shipped to ORNL. There was a spent fuel working group and a borosilicate glass working group. Activities that were to be handled by the borosilicate glass group will be handled by the Waste Acceptance Committee (WAC). The CEC inter-laboratory test is proceeding on schedule and testing should be completed by August 1988. A progress meeting for all participants was held at the Fraunhofer Institute, Wurtzburg, FRG in April, 1988. Three papers were submitted for presentation at the Materials Research Society Meeting in West Berlin in October, 1988. The ASTM version of MCC-1 was revised in response to two negative votes.

Preparation for acquisition of ATM-107, stainless steel clad spent fuel, was started. Criteria for selection are that the fuel be as representative as possible as the entire stainless fuel population and that the fuel acquisition should be reasonable practical. Four potential sources of ATM-107 were identified.

Microprobe analysis of spent fuel gave concentrations of 6.5 percent and 5.5 percent for U and Pu, respectively, and this was higher than the concentration of these elements predicted by ORIGEN. The average composition of Xe was 0.33 wt. percent which was 22 percent lower than the concentration predicted by ORIGEN. This could be due to surface release of Xe during preparation or a contribution of Xe at the fuel edge which was not included in the result. The average Cs concentration was 0.32 percent which is 60 percent above the ORIGEN predicted value, and the reason for this is not known.

D. Support to the Salt Repository Project

Work had been conducted earlier to develop a pH sensing electrode, and pH and Eh reference electrodes for use in high-temperature brine. There were no experimental activities, and a report, "Electrodes Development and Experimental Results," was completed. Closeout work was completed.

E. Support to the Basalt Waste Isolation Project

Tests were completed on ATM-11, a simulated Savannah River production glass was completed, and samples are being analyzed. All further activities on this project have ceased. Closeout work is proceeding, and activities are underway for dismantling, decontamination and cleaning of the laboratory.

F. Support to the Defense HLW Technology Program

The MCC program manager participated in a defense waste technology management (DWTM) meeting, where an approach for QA strategy for DWTM was developed. The MCC proposed to conduct experimental confirmation of certain key data necessary for obtaining approval for start-up of the Defense Waste Processing Facility. Data entry in the Comprehensive Data Base is continuing and additional data from the Catholic University of America, the Savannah River Laboratory, and the Hanford Waste Vitrification Project. The outline for the hard copy of this data base was given in a previous report (NUREG/CR-4735, Vol.3, p. 22, 1987).

G. Support to the Defense Waste Processing Facility

a. Product Consistency Test Round Robin.

The eight laboratories that participated in this test are Argonne National Laboratory, Penn State, Corning Glass Works, Pacific Northwest Laboratory, Catholic University of America, University of Florida, Savannah River Laboratory and the MCC. The test matrix included in the protocol calls for triplicate tests, conducted over three weeks instead of at the same time of four different specimens; two supplied by Savannah River, one supplied by NIST, and ARM-1. Replicate analyses of leachate samples also are specified. The test protocol specifies the tests to be conducted, the method of performing the tests, and the method of reporting the data to the MCC. Test kits include all materials except the deionized water, and these kits were sent to the participants in April.

b. DWPF Canister Impact Testing.

Test plans were developed for DWPF impact tests and include pre-impact dimension measurements, strain circle application and analysis, the impacting of canisters, preparation for helium leak testing and helium and dye-penetrant testing. Formulation of these test plans will permit testing to proceed without delay when the canisters are received from Savannah River. Seven canisters were received from Savannah River in April and helium leak testing of each canister was completed. This test provides data regarding the leak tightness of the closure weld and also serves to show if a leak existed prior to impact testing. The initial set of impact tests, done at 7-meters (23-feet) vertical drop, was carried out in mid May. The second set of impact

tests on the same canisters (7-meter drop on the top corner) was conducted in late June. After the second test, canister necks were pushed into the hollow plenum, but visual examination revealed no failure of any of the canisters. Canisters are undergoing further examination and analysis after the second test.

Analysis of the canisters after the initial set of tests showed that bottoms of the canisters were flattened, there were slight diameter increases, but no gross deformation was observed.

The strain was less than 5 percent, the minimum amount measurable by the strain circle method. All canisters were leak tight based on a tightness criterion of 1×10^{-6} atm-cc/s. Dye-penetrant tests showed no evidence of cracking in the welds. Dimensional changes in the canisters after testing were given as follow.

<u>Distance from bottom, cm</u>	<u>Canister Diameter, Increase, cm</u>	<u>Canister Diameter, Increase, %</u>
51	1.24	2.1
10.2	0.79	1.3
15.2	0.30	0.48
25.4	0.11	0.19
45.7	0.09	0.15

Canister height decrease in inches was 0.86 and percent of canister height decrease was 0.29.

c. Quality Control Guidelines.

A draft of "QA/QC Guidelines for Analytical Laboratory Practices for Application in the Nuclear Waste Repository Program" was completed and presented for discussion at the Analytical Methods Workshop. There were diverse opinions and additional review and submission of comments is expected.

d. The Comprehensive Data Base.

The data base covers a number of tasks but is described under this activity. As mentioned earlier, the hard copy of the data base was given in a previous report (ref. 1), and three major blocks of data for entering have been received from Catholic University of America (CUA), the Hanford Vitrification Project and Savannah River. Literature searching for individual papers was stopped due to funding limitations.

H. Support to West Valley Demonstration Project

a. Reference Glass Chemical Durability Testing.

Thirteen 28-day partial leachant exchange periods with ATM-10 have been completed. Boron releases were constant within 5 percent for periods 9 through 12 but the 13th period had an 8 percent decrease in boron indicating that steady state leaching of this material has not occurred. Eight 28-day partial leachant exchange tests have been conducted with the CUA glass (WVCM 50), and boron releases are rising at a rate of 5 percent per period. These pulsed-flow tests will continue until approximately twenty 28-day leachant exchange periods have been completed for each glass. Some of the data from the MCC-3 pulsed-flow tests are nearly identical with data from the MCC-1 static leach tests for the ATM-10 and the CUA glasses. MCC-1 tests of ATM-10, CUA (WVCM 50) and CTS (SF-6) glass show that the ATM-10 and the CUA glass were more durable than the CTS (SF-6).

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

Plans, preparation and the first melting of a synthetic West Valley sludge glass have been done. This glass contains sludge, Thorex and loaded zeolite. This glass will be leach tested using MCC-1 and MCC-3 and will be characterized in terms of composition, homogeneity, microstructure and redox state. Foaming of the sludge mixture could be a problem, and further tests are planned to determine ways that foaming can be controlled.

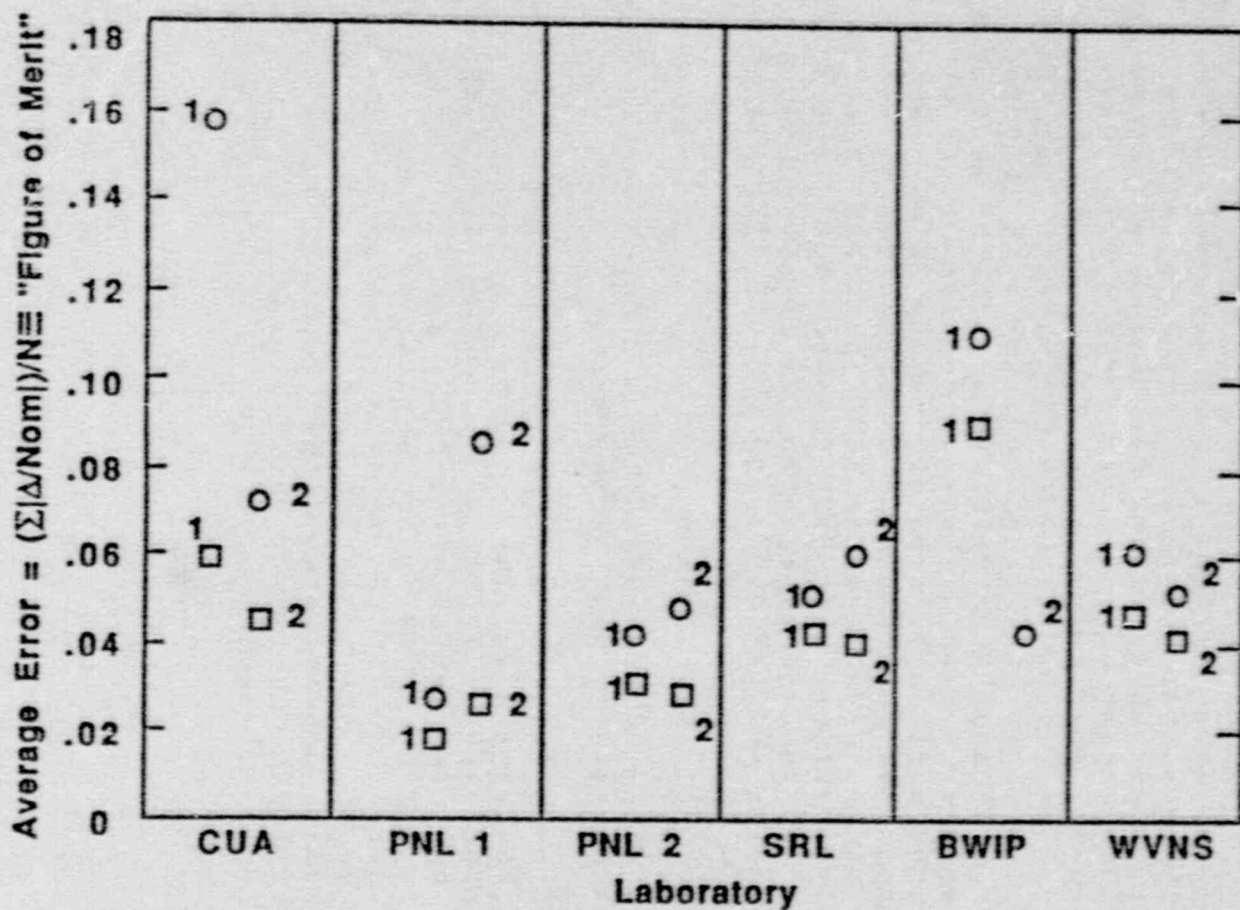


FIGURE 1. Comparison of Analytical Data From Round Robins 1 & 2
(O, □ = Duplicate Samples)

TABLE 1. Analytical Results Reported for MCC Waste Glass Interlaboratory Comparison - Fall 1987

Oxide	Average and (Standard Deviation) Weight Percent [†] Reported									
	Nominal Composition	Hahn-Meitner	Catholic University	PNL 1A	PNL 1B	PNL 2	SRL	BWIP	WVNS	Overall Mean
Al ₂ O ₃	6.285 (0.015)	5.849 (0.094)	6.180 (0.104)	6.183 (0.023)	6.219 (0.122)	6.347 (0.346)	6.078 (0.358)	5.770 (0.030)	6.141 (0.149)	6.096 (0.065)
B ₂ O ₃	10.326 (0.022)	10.212 (0.160)	10.001 (0.051)	10.303 (0.040)	10.432 (0.222)	----- (-----)	10.451 (0.342)	----- (-----)	10.781 (0.334)	10.363 (0.102)
BaO	0.295 (0.000)	0.292 (0.007)	0.287 (0.009)	0.296 (0.002)	0.286 (0.006)	0.245 (0.003)	0.298 (0.008)	----- (-----)	0.293 (0.031)	0.285 (0.006)
CaO	1.275 (0.006)	1.172 (0.029)	0.803 (0.097)	1.174 (0.015)	1.335 (0.044)	1.183 (0.051)	1.494 (0.067)	1.250 (0.030)	1.145 (0.040)	1.195 (0.066)
CeO ₂	0.732 (0.002)	----- (-----)	0.474 (0.021)	0.716 (0.016)	0.685 (0.058)	0.642 (0.004)	----- (-----)	0.480 (0.000)	0.645 (0.115)	0.607 (0.038)
Cr ₂ O ₃	0.157 (0.001)	0.172 (0.007)	0.162 (0.002)	0.166 (0.004)	0.171 (0.007)	----- (-----)	0.159 (0.003)	----- (-----)	0.154 (0.022)	0.164 (0.003)
Cs ₂ O	0.482 (-----)	----- (-----)	0.487 (0.008)	0.306 (0.023)	0.306 (0.023)	0.441 (0.002)	0.374 (0.023)	----- (-----)	0.483 (0.026)	0.400 (0.036)
Fe ₂ O ₃	7.009 (0.042)	6.984 (0.160)	7.092 (0.023)	7.002 (0.040)	6.685 (0.144)	6.985 (0.198)	6.829 (0.298)	7.160 (0.040)	7.073 (0.041)	6.976 (0.058)
K ₂ O	2.156 (0.030)	2.083 (0.024)	2.299 (0.032)	1.919 (0.021)	1.483 (0.096)	2.112 (0.049)	1.809 (0.222)	2.040 (0.000)	2.184 (0.069)	1.991 (0.098)
La ₂ O ₃	0.011 (0.000)	----- (-----)	0.024 (0.001)	0.017 (0.001)	0.016 (0.001)	0.008 (0.001)	----- (-----)	----- (-----)	----- (-----)	0.016 (0.004)
Li ₂ O	3.771 (0.014)	3.597 (0.076)	3.768 (0.081)	3.598 (0.061)	3.662 (0.070)	----- (-----)	3.483 (0.145)	----- (-----)	3.791 (0.086)	3.650 (0.047)

TABLE 1. (Continued)

Oxide	Nominal Composition	Hahn- Meitner	Catholic University	PNL 1A	PNL 1B	PNL 2	SRL	BWIP	WVNS	Overall Mean
MgO	0.713 (0.004)	0.695 (0.010)	0.744 (0.010)	0.663 (0.014)	0.711 (0.018)	----- (-----)	0.679 (0.051)	0.780 (0.000)	0.750 (0.007)	0.717 (0.015)
MnO ₂	0.747 (0.005)	0.677 (0.032)	0.745 (0.005)	0.774 (0.004)	0.769 (0.017)	----- (-----)	0.712 (0.020)	0.750 (0.030)	0.608 (0.007)	0.719 (0.026)
MoO ₃	0.753 (0.005)	0.730 (0.031)	0.792 (0.013)	0.740 (0.010)	0.728 (0.019)	0.725 (0.002)	0.784 (0.043)	----- (-----)	0.718 (0.025)	0.745 (0.010)
Na ₂ O	10.081 (0.030)	9.868 (0.153)	11.283 (0.046)	9.177 (0.056)	9.963 (0.380)	----- (-----)	10.023 (0.275)	9.630 (0.070)	10.504 (0.256)	10.064 (0.245)
Nd ₂ O ₃	2.440 (0.009)	2.275 (0.044)	1.343 (0.018)	2.324 (0.012)	2.457 (0.071)	----- (-----)	----- (-----)	----- (-----)	2.268 (0.228)	2.133 (0.170)
NiO	0.190 (0.002)	0.192 (0.007)	0.194 (0.006)	0.197 (0.004)	0.199 (0.005)	0.196 (0.006)	0.551 (0.137)	0.240 (0.000)	0.223 (0.016)	0.249 (0.052)
P ₂ O ₅	1.662 (0.010)	1.600 (0.000)	----- (-----)	2.140 (0.522)	1.246 (0.278)	----- (-----)	1.700 (0.134)	1.700 (0.040)	1.762 (0.121)	1.691 (0.138)
RhO ₂	0.006 (0.000)	----- (-----)	----- (-----)	----- (-----)	----- (-----)	0.005 (0.001)	----- (-----)	----- (-----)	----- (-----)	0.005 (-----)
RuO ₂	0.044 (0.000)	----- (-----)	0.019 (0.001)	----- (-----)	----- (-----)	0.040 (0.001)	0.071 (0.005)	----- (-----)	0.075 (0.010)	0.051 (0.014)
SO ₃	0.138 (0.002)	0.172 (0.016)	----- (-----)	----- (-----)	----- (-----)	----- (-----)	----- (-----)	----- (-----)	0.183 (0.041)	0.177 (0.007)
SiO ₂	47.213 (0.235)	47.405 (0.419)	48.986 (0.075)	47.952 (0.723)	46.728 (1.221)	46.487 (0.802)	44.650 (1.658)	47.700 (0.000)	47.203 (0.295)	47.139 (0.127)

TABLE 1. (Continued)

Oxide	Nominal Composition	Hahn- Meitner	Catholic University	PNL 1A	PNL 1B	PNL 2	SRL	BWIP	WVNS	Overall Mean
SrO	0.204 (0.000)	0.197 (0.010)	0.185 (0.009)	0.210 (0.001)	0.195 (0.002)	0.191 (0.002)	0.203 (0.007)	----- (-----)	0.191 (0.009)	0.196 (0.003)
TiO ₂	1.888 (0.006)	1.848 (0.037)	2.007 (0.023)	1.916 (0.019)	1.878 (0.040)	1.583 (0.059)	1.923 (0.105)	1.890 (0.030)	1.953 (0.019)	1.875 (0.042)
Y ₂ O ₃	0.011 (0.000)	----- (-----)	0.011 (0.000)	----- (-----)	0.014 (0.001)	0.012 (0.001)	----- (-----)	----- (-----)	----- (-----)	0.012 (0.001)
ZnO	0.608 (0.002)	0.553 (0.016)	----- (-----)	0.591 (0.005)	0.586 (0.008)	0.551 (0.020)	0.658 (0.032)	----- (-----)	0.594 (0.013)	0.589 (0.016)
ZrO ₂	1.626 (0.006)	1.435 (0.005)	1.548 (0.042)	0.567 (0.223)	0.537 (0.223)	1.588 (0.007)	1.545 (0.075)	1.680 (0.020)	1.511 (0.018)	1.301 (0.185)

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11. ABSTRACT (200 words or less)

This report summarizes evaluations by the National Institute of Standards and Technology (NIST) of Department of Energy (DOE) activities on waste packages designed for containment of radioactive high-level nuclear waste (HLW) for the six-month period February 1988 through July 1988. Activities for the DOE Materials Characterization Center are reviewed for the period January 1988 through June 1988. A summary is given of the Yucca Mountain, Nevada, disposal site activities. Short discussions are given relating to the publications reviewed and complete reviews and evaluations are included.

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Tuff	Borosilicate Glass
Spent Fuel	Irradiation
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Basalt	Leaching
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