See pocket 1 for encl.

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

August 31, 1987

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

Dear Mr. Wick:

Enclosed is a Draft Biannual Report for the project "Evaluation and Compilation of DOE Waste Package Test Data" (FIN-A-4171-7). Comments by your staff and contractors are requested as soon as is practical, so that complete responses by NBS staff can be prepared and incorporated in a timely manner.

Please call me if you have any questions concerning this work.

Sincerely,

Charles G. Interrante

Charles G. Interrante
Program Manager
Corrosion Group
Metallurgy Division

Enclosures

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NUREG/CR-4735
Volume 3

# EVALUATION AND COMPILATION OF DOE WASTE PACKAGE TEST DATA

DRAFT BIANNUAL REPORT
Covering the Period February 1987 to July 1987


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August 31, 1987

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## EXECUTIVE SUMMARY

This is the third biannual progress report on the National Bureau of Standards (NBS) assessments of the Department of Energy (DOE) activities related to the waste package for disposal of radioactive high-level waste (HLW). It contains NBS reviews conducted over the period February 1, 1987 to July 31, 1987 on DOE reports. Status reports given here highlight the NBS assessments of DOE activities.

Eleven reviews of publications resulting from DOE-sponsored work in NNWSI (Nevada Nuclear Waste Storage Investigations) during this six-month period are divided into four categories: Zircaloy, copper, spent fuel, and glass. Three issues are emphasized. These deal with the possibility of stress-induced failure of Zircaloy, the possible high corrosion of copper and copper alloys, and the lack of site-specific characterization data.

In two previous biannual NBS reports, the major deficiencies in the available data pertaining to a waste repository in basalt (BWIP -- Basalt Waste Isolation Project) were noted with specific emphasis placed on the corrosion resistance of the candidate waste-package container materials. Four evaluations completed during this period indicate the following: AISI 1020 steel, a candidate waste-canister material, exhibits both localized corrosion and environmentally assisted cracking behavior at elevated temperatures (150°C), when immersed in basalt repository-like groundwater. If this material is to receive further consideration, much more work is required. Improvements to the simulation of repository environments for laboratory studies have been made. However, more data are needed to verify the exact chemical reactions to be expected to occur under repository conditions.

For the Salt Repository Project (SRP), an overview of the Deaf Smith site, and its potential problem areas, points up the importance of the duration of corrosion tests and some of the conditions that may preclude prompt initiation of needed long-term testing. Five reviews of SRP reports are presented. Three are concerned with colloidal sodium. A fourth on corrosion of A-216 demonstrates the considerably higher corrosion rates associated with high-magnesium brines. A fifth review concerns buckling of a container and it highlights the importance of mechanically induced stress on local corrosion processes.

A summary of the activities of the Crystalline Repository Project is given to complement the coverage of other DOE project offices. In addition to the sites that may be available from the first repository program and other sedimentary rock geologic formations not previously considered, crystalline rock is the primary geologic media under consideration for the second repository. Crystalline rock formations are located in 17 states in the north-central, northeastern, and southeastern regions of the United States.

Both the schedule and any site-specific activities for the second repository have been delayed. Nevertheless, the U.S. Department of Energy continues to cooperate with international groups (IAEA, NEA, and CEC), which are doing important research related to repositories in granite and crystalline rock formations.

Technical exchange meetings were held at two sites expected soon to produce vitrified HLW, the West Valley Demonstration Project (WVDP) and the Defense Waste Processing Facility (DWPF). These meetings concluded with the understanding that technical discussions in greater depth and sharper focus would be needed to keep abreast of current developments. The principal concerns are (1) verification of the composition of production runs and (2) leaching characteristics (in actual repository environments) of the specified glass composition.

Reviews of several reports on glass leaching are included here and many more have been initiated but not yet completed. The leaching characteristics of vitrified HLW can be affected by various factors, principal among which are the composition of the glass used to vitrify the HLW and the environment in which the leaching may take place. Repository environments are simulated in laboratory tests. Refinements in these simulated repository conditions are suggested, so as to assure that leach rates in a repository do not significantly exceed those predicted from the laboratory tests. In leaching of glass, a preliminary assessment of the role of redox potential (Eh) leads to the conclusion that solutions of a more reducing nature are less aggressive. This suggests that repositories in which reducing conditions persist in the vicinity of the waste package would be favorable, with low leaching rates of vitrified waste.

Pertinent activities of the Materials Characterization Center were summarized and included here in eight categories, which correspond to categories of the MCC's monthly reports. These are Program Administration, Quality Assurance (QA), and support to various offices: the Office of Geologic Repositories, the Salt Repository Project (SRP), the Basalt Waste Isolation Project (BWIP), the Defense HLW Technology Program (DP-12), the Transportation Technology Center (TTC), and the West Valley Demonstration Project (WVDP). It appears that increased support and cooperation on the part of all repository offices and other pertinent DOE offices is needed.

This to enable MCC to meet their objectives of ensuring materials data are available on waste materials, by developing standard test methods, testing waste (and other) materials, and publishing the Waste Materials Handbook.

An NBS alternate interpretation of published data is given here to stress the benefit and necessity of independent interpretation of data to be used to predict the performance of materials proposed for use in a nuclear waste package. This illustration contrasts published results with results obtained from an alternate NBS interpretation of the same data. A conclusion reached from the alternate analysis is that leach rates of glass recommended in the original report would be improved by changing the recommended composition, in particular, by substitution of $Al_2O_3$ for $Na_2O$.
An appendix on the NBS/NRC Data Center activities describes various software enhancements developed recently to aid in data handling and retrieval. For data retrieval, it highlights a menu system suitable for both novice and experienced users.

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## 1.0 INTRODUCTION

Current NBS activities related to reviews and evaluations of the Department of Energy (DOE) waste-package activities are detailed in this biannual report. Reviews related to research performed for the three DOE project offices, the Nevada Nuclear Waste Storage Investigations (NNWSI), the Basalt Waste Isolation Project (BWIP), and the Salt Repository Project (SRP) are discussed in sections two through four, respectively.

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, New York and the Defense Waste Processing Facility (DWPF) located at the Savannah River Plant in Savannah, Georgia are expected to vitrify HLW in the near future. NBS activities in this area have continued to increase with six reports being reviewed during this reporting period. The work on glass is presented in section 5. In section 7, an illustration of the uncertainties in the choice of glass composition is given to illustrate the importance of independent interpretation of data.

Activities of the DOE-sponsored Materials Characterization Center for the period January 1, 1987 through June 30, 1987 are discussed in section 6.

While DOE work sponsored to date has focused on the first repository, the second repository is still a viable part of the Nuclear Waste Policy Act of 1982, and a discussion of the current status of the second repository program is included as section 8.

Draft NBS reviews and evaluations conducted over the period February 1, 1987 through July 31, 1987 are included as Appendix A; contributing reviewers for these works are acknowledged as a group on the cover page of this report. As reviews are completed and approved for publication, they are included in the NBS/NRC Database for Reviews and Evaluations on High-Level Waste Data. One of the NBS goals is to make this database "user friendly". The system is designed so that it is easy for the novice searcher to find relevant information quickly and with a minimum of effort and training. Appendix B contains information on database activities for the period covered in this report.

Studies involving laboratory testing at the NBS are continuing in four areas, but no reports on this work are given here. 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.

## 2.0 NNWSI - NEVADA NUCLEAR WASTE STORAGE INVESTIGATIONS

One of the three proposed nuclear-waste repository sites is located in the Yucca Mountains of Nevada about 100 miles northwest of Las Vegas. The Environmental Assessment published by the Department of Energy (DOE) describes a repository located 400 m below the surface and 100 m above the water table. Tuff, the geologic formation found here, is composed of a dry, compacted volcanic ash.

Eleven reviews were concluded during this reporting period, and three issues of concern will be emphasized. Briefly, these concerns deal with the possibility of stress-induced failure of Zircaloy, the possible high corrosion of copper and copper alloys, and the lack of site-specific characterization data.

The reviews of publications resulting from DOE-sponsored work in NNWSI during this six-month period are divided into four categories as follows: 1) Zircaloy, 2) copper, 3) spent fuel, and 4) glass. Each will be discussed within its own category, followed by a general discussion of other important issues not necessarily identified in these reviews.

### 2.1 Zircaloy

Radioactive fuel, in the form of small cylinders, is clad (encased) in a thin-walled Zircaloy sleeve. Failure of the Zircaloy sleeve allows the escape of radioactive material. Thus, two important areas of research are the causes of failure of the sleeve and the rate of dissolution of the radioactive waste after this cladding has been breached.

Two publications describe plans for future experiments designed to provide information on the corrosion reactions of Zircaloy for two simulated repository conditions [Smith, 1986a; Smith 1986b]. The first condition simulates that period in the life of a repository after 90 to 100 years of closure, and it assumes an unbreached canister holding breached Zircaloy-clad fuel rods. The second condition simulates the period 1000 years after closure, and it assumes a breached canister and breached fuel rods. Information on the progress of the corrosion reactions will be obtained from chemical analysis of water samples in which the materials are immersed. Samples are taken periodically throughout the experimental periods (2, 6, and 12 months). Examination of the corroded surfaces after the experiments may include metallographic examination using light microscopes, scanning electron microscopy, and Auger techniques. Whereas these experiments will provide valuable information, they could be improved by including other measurements, such as electrochemical polarization, a. c. impedance, and other appropriate electrochemical measurements [Smith, 1986b].

In the second report, Smith describes an experimental plan in which the stress corrosion failure of Zircaloy is studied. C-rings machined from "defueled" Zircaloy cladding are loaded to an unspecified stress level and exposed to the same environments described in the previous experiment. This test procedure does conclusively reveal the susceptibility of Zircaloy to stress corrosion cracking (SCC) because failure may occur through other means. Hydride formation, for example, may embrittlement the alloy and lead to failure. In the absence of failure in the proposed tests, slow-strain-rate measurements would provide a more severe test of susceptibility to SCC [Smith, 1986a]. Other workers have shown embrittlement of Zircaloy in gaseous iodine at 350°C with increased tendency to failure at low oxygen concentrations [Gangloff, 1979].

The third report in this section, "Attachment 1 to Letter Dated 8 March 1985 to M. Steindler, Argonne National Laboratory," is an early listing of a variety of proposed experiments and experiments in progress [Ballou, 1985].

## 2.2 Copper

Prior to emplacement in a repository, fuel rods will be placed in metal canisters that will facilitate handling and, thereby, prevent the movement of radioactive waste into the environment after the repository is closed. Copper is one of the metals being considered as a container material, and information on the rate of corrosion of copper in a tuff environment is important.

The first reference by L. B. Ballou and R. D. McCright, is an early description of plans for the testing of copper as a possible canister material. Implementation of these plans resulted in two-year study, which concludes that copper and two of its alloys appear to be good candidates for possible use as canister materials, but this report cautions that the effects of gamma radiation on the corrosion behavior of these metals has not been addressed [Ballou, 1986]. The authors point out that nitric acid is severely corrosive to copper and copper alloys, even in fairly dilute solutions of nitric acid. This consideration becomes extremely important because other workers, Van Konynenburg in 1986 and Abrajano in 1986, have indicated that nitrogen fixation by gamma radiation will lead to the formation of nitric acid [Abrajano, 1986; Van Konynenburg, 1986].

## 2.3 Spent Fuel

Once the Zircaloy sleeve (or cladding) of a fuel rod is breached, the release of radionuclides can occur. If the metal canister holding the fuel rods is also breached, moisture can contact the spent fuel. In the presence of moisture, dissolution of the spent fuel and the release of radionuclides follows. The oxidation state of the spent fuel affects the rate at which this dissolution will take place. Oxidation is one of many important factors in this process.

Oxidation of spent fuel contained in breached Zircaloy cladding can increase the solubility and concentration of specific radionuclides. Einzinger describes a series of tests to measure the degree of oxidation of spent fuel under various conditions of exposure (temperature, moisture, time). However, it is not clear whether the authors have taken into consideration the increased vapor pressure of water at elevated temperatures. An increase in vapor pressure could result in oxidation rates considerably different from those in dry air [Einzinger, 1986].

The rules and regulations for licensing a high-level nuclear waste repository, as set by NRC and EPA, are discussed by Oversby in UCRL-94659. Site-specific performance-assessment calculations are necessary in order to compare the behavior of the waste form under the conditions of exposure for all proposed sites. Oversby reviews the factors that affect radionuclide release rates, and identifies six areas where new data are needed [Oversby, 1986].

## 2.4 Glass

Another way in which DOE plans to dispose of HLW is to vitrify it in borosilicate glass and these vitrified waste materials will be placed in metallic canisters. The effects of radiation on this vitrified waste and its subsequent solubility are important.

Theoretical modeling calculations on the effects of radiation on waste glass described by Van Konynenburg result in reasonable agreement with experimental observations. On the basis of these modeling calculations, it is shown that the principal reactions result in the formation of $H_2$, $O_2$, $NO_2^-$, $NO_3^-$, and $H^+$ [Van Konynenburg, 1986]. Abrajano, et al., describe a more recent compilation of experimental data on which the modeling calculations of the Van Konynenburg reference are based in part. These experimental data emphasize that an important reaction during the irradiation of moist air is the production of nitric acid. However, dissolution of the glass waste and buffering action of the bicarbonate in tuff tend to limit the effect of the nitric acid to a pH of 6.4. The effect on glass dissolution is less than originally expected [Abrajano, 1986].

UCRL-15723 and ANL-85-41 describe a test for measuring dissolution of radionuclides in unsaturated repository conditions. J-13 water is dripped onto a radionuclide-doped glass form in a tuff cup. Analysis of leachate provides information on the rate of radionuclide dissolution. Local dissolution of the stainless-steel waste holder increased the rate at which the matrix breaks down with increased rate of radionuclide release [Bates, 1985; Bates, 1986].

## 2.5 Additional Discussion

Of the three proposed sites proposed for the first repository, Yucca Mountain is unique in its low moisture content and oxic conditions. In addition, availability of soluble salts is low, and this results in a relatively noncorrosive environment. However, information on this site is based on data obtained from the surrounding land. At this time, the lack of site-specific characterization data may be the most crucial shortcoming in the program. It is on these data that critical decisions affecting the future of the NNWSI program are based.

Some of the most important information such as the composition of soluble salts in the water is questionable. Present information on water composition for this site has been assumed to be like that of J-13 well water taken from a point several miles from the proposed repository site [DOE, 1986b]. Composition of the electrolyte bears directly on the leaching or corrosion processes by which the glass or the metallic components of a waste package will be degraded.

Well water in the compacted tuff travels through fractures and other large, interconnected imperfections in the geological formation. Pore water, held in the interstices and pores of the rock, is relatively immobile. The lack of fractures and freely flowing water in the tuff at this site make the composition of pore water all the more important. While the composition of the pore water is unknown, it is very likely that the pore water is the most abundant water at the tuff site.

# 3.0 BWIP -- BASALT WASTE ISOLATION PROJECT

In two previous biannual NBS reports, the major deficiencies in the available data pertaining to a waste repository in basalt were noted with specific emphasis placed on the corrosion resistance of the candidate waste package container materials [Interrante, 1987a; Interrante, 1987b]. In the past six months, several reports on corrosion studies have been received at NBS and formal evaluations of them have been initiated. Four of these evaluations have now been completed and their results follow.

Anantatmula studied the corrosion behavior of AISI 1020 hot-rolled steel packed in 75 percent basalt, 25 percent bentonite (the packing material mixture proposed for the future repository in basalt) while immersed in various liquids [Anantatmula, 1984]. Twelve different tests were performed (six at 100°C and six at 200°C) using liquids comprised of deionized water and various combinations of $Cl^{-1}$, $F^{-1}$, $SO_4^{-2}$ , and $CO^{-2}$ ions; and weight losses were measured after four weeks immersion. A Plackett-Burman statistical analysis method was used to determine the significant variables. In addition, the exposed metal surfaces were studied by optical metallography, scanning electron microscopy, and X-ray diffraction. Only temperature, not the liquid chemistry, was found to be a significant variable here. However, since only twelve tests were run, and without replicate samples, the statistical relevance of this test is extremely limited. Higher corrosion rates were measured at 100°C than at 200°C, consistent with previous findings. It was concluded that the formation at higher temperatures of a partially protective iron-rich clay (iron saponite) on the surface of the metal caused this anomalous behavior [Anantatmula, 1984]. However, the corrosion mechanism is also undoubtedly different at the two temperatures as evidenced by the authors' finding the magnetite form of iron in the corrosion product of only the high-temperature tested samples. This result has not received much attention in the past and it certainly warrants further investigation.

In 1984 a study was completed by Brehm, Lutton, Rivera, Maffei, Bohringer, Paine, and Pingel concerning of the metallic corrosion likely to occur in a basalt repository. A series of 48 test specimens at 100°C and 200°C of Fe-9Cr-1Mo steel (normalized and tempered) were immersed for one month in liquids containing various concentrations of sulphate, carbonate, fluoride, and chloride ions; and weight loss measurements were performed [Brehm, 1984]. Unfortunately, the data measured in this initial well-planned study were not sensitive enough to indicate any general trends in the effects of either temperature or electrolyte on the corrosive attack of this steel. Further studies using more sensitive equipment were initiated. In this same study, the electrochemical passivation characteristics of various proposed waste-container materials immersed in synthetic Grande Ronde groundwater were studied. Similar types of passive regions (although at different potentials) were found for AISI 1020 steel, Fe-9Cr-1Mo steel, and cupro-nickel

(90Cu - 10Ni). However, only the passive region for the AISI 1020 steel was specified; and it was measured to exist at potentials between -0.5 and -0.25 volts. For higher potentials than these, the AISI 1020 steel was observed to develop pits. The pitting behavior of the other steels will be the subject of a future report by these authors.

Pitman conducted a series of 20 slow-strain-rate tests conducted at two different extension rates and at two different temperatures on AISI 1020 wrought steel (one of the candidate waste-package container metals) plate either in air or immersed in synthetic Grande Ronde groundwaters. The presence of environmentally assisted cracking (EAC) processes occurring in this material at 150°C was indicated by a significant decrease in the reduction in cross-sectional area (RA) measured for the material tested at the lowest strain rate ($2 \times 10^{-7}$/s) while immersed in groundwaters from that measured when the material was similarly tested in air. Highly stressed regions (e.g. machined edges, sample grip areas, necked regions) of those specimens exhibiting the reduced RA values were also found to exhibit pitting attack. The fracture surfaces of these low-ductility samples also showed evidence of EAC, which was indicated by the presence of intergranular fracture, transgranular cleavage, and secondary cracking [Pitman, 1983].

Jantzen conducted a simulation study of the redox potentials likely to exist in a waste repository in basalt. Since redox potentials are important to the determination of what chemical reactions will occur in a system, such information is needed for both corrosion and leaching studies. Simulation of the basalt repository Eh-pH conditions was found in this investigation to be easily achievable when crushed basalt was used as an additive to deionized water. This is far more preferable than a previous method of adding hydrazine (a substance foreign to the repository) to the liquid environment. However, even though the above method is good for achieving the proper Eh values, care must still be exercised in the measurement methods used to obtain these data. Care must also be exercised in using these data to determine the extent of reactions likely to occur. This study points out the large difference in redox potentials between oxic and anoxic solutions and the consequential differences in waste-form leaching behavior. Under oxic conditions the presence of iron was also found to significantly enhance the leaching of a waste glass, SRL 165 [Jantzen, 1984].

In conclusion, it appears that the candidate waste canister material, AISI 1020 (hot rolled) wrought steel, exhibits both localized corrosion and environmentally assisted cracking behavior at elevated temperatures (150°C) when immersed in basalt repository-like groundwater. It is possible that this material's reduced general corrosion rate at the higher temperatures may also be related. If this material is to receive further consideration, much more work is required, especially in the areas of establishing conservative "time-to-failure" values. Further work on different thickness-rolled plate (with its different microstructure) and on weldments is also needed. Improvements to the simulation of repository environments for laboratory studies have been made. However, more measured data is needed to verify the exact chemical reactions to be expected to occur under repository conditions.

## 4.0 SRP - - SALT REPOSITORY PROJECT

The Deaf Smith site is in the southern high plains of the Texas panhandle, 35 miles southwest of Amarillo in the north-central part of Deaf Smith County. Deaf Smith County is composed primarily of cropland with some range land and has a population density of about four people per square mile. The site will consist of nine square miles and acquisition of the initial 61 acres required for site characterization is projected to be completed in 1987. The formal process of site characterization has begun and is projected to be completed in 1988.

The host rock of the repository is 2400 to 2500 feet below the surface and approximately 1000 feet below the aquifer that supplies much of this region with irrigation water. The host rock is bedded rock salt approximately 160 feet thick. The rock salt bed is the result of the drying of a salt lake during the Permian Age. As a result, the salt bed may contain varying amounts of impurities and included water. However, bedded rock salt has numerous advantages that lead to the selection of a salt bed site including the following:

- Deposits are deep, thick and laterally extensive
- Deposits occur in areas of low seismic activity
- Deposits have remained undisturbed for $10^7$ to $10^8$ years
- High thermal conductivity
- Low permeability
- Readily deformed plastically
- Good radiation and shielding properties

After evaluation of salt domes and salt beds over the United States, the Deaf Smith site in May 1986 was selected for further study and characterization.

## 4.1 Potential Problem Areas

Land Acquisition -- In May 1986, when this site was selected for further study and characterization, all of the land at the site was privately owned. Acquisition of the land is under way and needs to be completed so that actual characterization of the site can proceed. Condemnation proceedings, if required, could delay site characterization. This would delay corrosion testing and decrease the available time for testing.

On-Site Characterization -- It is important to thoroughly characterize the salt environment and begin long-term corrosion testing on the entire range of expected environments as soon as possible. The accuracy of corrosion rate estimates and extrapolations used in making lifetime predictions of the container may be greatly affected by the duration of the tests.

Container Alloys -- At present, the primary candidate alloy for the waste container is A216 Steel. The reasons for the selection of this alloy and reservations with this selection have been discussed by NBS workers in previous reports [Interrante, 1987a; Interrante, 1987b]. Alloy selection was based on the assumption that, if uniform corrosion of the alloy proceeds uninhibited, then other corrosion-related failure mechanisms could be ignored. Localized corrosion, stress corrosion cracking, and hydrogen embrittlement are potential failure modes that must be evaluated by mechanistic modeling and/or experimental observations, and not by assumption.

The alternate alloy for container fabrication is Ti-code 12. Ti-code 12 was selected because of its corrosion resistance. The corrosion resistance of this alloy is the result of the formation of a passive film. As a result, the uniform corrosion assumption cannot be applied to this alloy. Also, Ti-code 12 is susceptible to hydrogen embrittlement and radiation-induced hydrogen evolution must be considered.

The limited-brine assumption is a critical issue in container alloy selection. If DOE can guarantee that only limited quantities of brine will can reach the containers, then alloys with very low resistance to corrosion can be used. However, if DOE is forced to assume unlimited brine, then more corrosion-resistant alloys must be considered.

## 4.2 Reviews

During the period covered by this report, five papers were reviewed which pertain to the Deaf Smith site.

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

(2) Levy, P. W., "Radiation Damage Studies on Natural Rock Salt from Various Geologic Localities of Interest to the Radioactive WAste Disposal Program," Nuclear Technology, 60, 1983, p. 231-243.

(3) Levy, P. W. and Kierstad, J. A., "Very Rough Preliminary Estimate of Colloidal Sodium Induced in Rock Salt by Radioactive Waste Canister Radiation," Materials Research Society Symposium Proceedings, 26, 1984, p. 727-734.

(4) Westerman, R. E., Haberman, J. H., Pitman, S. G., and Perrin, J. S., "Corrosion of Iron-Base Waste Package Container Materials in Salt Environments," PNL-SA-14029, March 1986.

(5) Mallett, R. H., "Buckling Design Criteria for Waste Package Disposal Containers in Mined Salt Repositories", BMI/ONWI-597, Swanson Engineering Associates Corporation, McMurray PA, December 1986.

The first three of these reports are concerned with the formation of sodium colloids as a result of irradiation of the rock salt surrounding the waste-storage container. Interest in the formation of colloidal sodium is due to concern over the influence of colloidal sodium on the chemistry of the environment around the container. However, most of the work has concentrated on the scientific basis of radiation-induced colloid formation and not the resulting changes in chemistry, transport and corrosion behavior.

The fourth report discusses corrosion of cast A-216 steel for waste-package containers with two different heat treatments. The tests were conducted under continuous exposure conditions (unlimited brine), which the authors consider "severe." The results show that considerably higher corrosion rates result from high Mg brines (containing 130 mg/l), which is the water composition expected in the salt beds [Westerman, 1984].

The fifth report concerns a mechanical failure mode and, as the authors point out, buckling is not really a failure mode, provided that the container integrity will still be preserved. Only the shape of the container will have changed. However, buckling of the container will result in high tensile stresses in the external surfaces of the container and this condition could lead to stress corrosion cracking or hydrogen embrittlement of the container.

## 5.0 VITRIFICATION OF HIGH-LEVEL WASTE

The processing and properties of the glass waste form will be critically important issues as the Nuclear Regulatory Commission (NRC) makes licensing decisions on facilities for vitrifying and disposing of high-level waste. The purpose of NBS activities in high-level-waste (HLW) vitrification is to provide the NRC with technical information necessary for making licensing decisions. This objective is accomplished primarily by technical assessments of work performed by DOE, its contractors, and other laboratories.

### 5.1 Technical Issues

The primary technical issues in HLW vitrification are reflected in three questions: (1) Will the facilities proposed by the Defense Waste Processing Facility (DWPF) and the West Valley Demonstration Project (WVDP) produce a glass of the composition to be specified, (2) how will the composition of glass poured during actual production run be verified, and (3) will the leaching behavior of the specified glass meet NRC criteria for radionuclide release.

During the current reporting period, much of the NBS activity in the HLW vitrification area has been directed towards the question of glass leaching. Several literature reports on glass-leaching studies have been reviewed, and a number of technical issues have been identified. Some of these issues are addressed below.

Glass leaching studies reviewed thus far indicate that the repository environment may have a significant effect on the rate of glass leaching. In general, the experimental evidence indicates that the leach rate may be lower in a repository than in laboratory tests. Because leaching studies at the candidate repositories are not now possible, improved laboratory and field simulations are an important means of predicting leaching behavior in the repositories. Papers reviewed during this reporting period, and work presented at the DWPF Technical Exchange Meeting discussed below, show an increased emphasis on simulated repository conditions in laboratory leaching studies. Simulations include, for example, rock cups used to hold the leachant and the glass sample. Pieces of the canister metal may also be added to this simulated environment. In principle, repository simulation tests can incorporate flow, but this variable has not been used in the simulation studies reviewed to date. These refinements make the tests potentially more reliable as indicators of behavior in real repositories. However, more detailed data on the hydrology and geology of the repository site will be needed to determine how well the simulation corresponds to the actual repository conditions. Thus, the issue of site characterization remains critical.

## 5.2 Reviews

Reviews of some key papers on the role of the redox potential (Eh) in glass leaching were completed as draft reviews. Background documents from Swedish research on this subject were also studied, and experts on Eh-pH (Pourbaix) diagrams were consulted to evaluate the work being carried out in the nuclear waste program. It was concluded (tentatively) that the basic qualitative conclusions of the work, i.e., that solutions of a more reducing nature are less aggressive in leaching the glass, appears to be valid. However, the experimental methodology and proper application of Eh, in describing the redox behavior of the leachant solutions, must be considered carefully in reviewing studies in this area.

Preliminary reviews of Chapters 1 and 7 of Pacific Northwest Laboratory Report PNL-5157, "Final Report of the Defense High-level Waste Leaching Mechanisms Program," were completed. Because of the importance of Chapter 1 as a summary of progress in glass leaching studies through 1984, a multiple review was conducted. Three independent reviewers have completed reviews which are being edited into a single, composite review. This composite review will then be returned to the reviewers for comments before being submitted for the formal NBS approval process. The preliminary review of Chapter 7 being expanded. A second reviewer has been added at the request of the first, to provide expertise in evaluating the results of modeling studies. A preliminary review of Chapter 4 of PNL-5157 has been started and is expected to be completed during August 1987.

## 5.3 Technical Exchange Meetings

Plants at West Valley, New York and Savannah River, South Carolina are currently developing technology and facilities for vitrifying HLW. The West Valley Demonstration Project (WVDP) deals with commercial HLW, while the Defense Waste Processing Facility (DWPF) at the DOE Savannah River Plant is working on defense HLW. Technical Exchange Meetings attended by NBS contractors and personnel, were held at both West Valley and Savannah River during this semiannual reporting period. These meetings are summarized briefly.

The WVDP Technical Exchange Meeting took place in West Valley on February 18-19, 1987. NBS attendees included Charles Interrante, Melvin Linzer, Ernest Plante and NBS consultants Bruce Adams and John Wasylyk. Talks were presented on the processing, physical properties, and leaching behavior of the waste-glass form. A tour of the facilities was conducted as part of the meeting.

A DWPF Technical Exchange Meeting was held at Savannah River on April 22-23, 1987. This meeting was attended by Charles Interrante and Dale Hall of NBS, and NBS consultants Bruce Adams and John Wasylyk. The meeting included tours of (1) Savannah River's HLW Waste Cave Laboratory, where small-scale processing studies are carried out, (2) the Equipment Test Facility, where canister decontamination, welding and scale melting procedures are developed, and (3) the DWPF construction site and scale model. Several technical presentations were also made. In the area of glass HLW forms, an overview of leaching studies was given. The overview was a useful update on the SRP's views on test methods and current understanding of glass leaching behavior.

The West Valley and Savannah River Technical Exchanges gave NBS participants an opportunity to broaden their knowledge of WVDP and DWPF activities and to discuss critical issues with DOE personnel and their contractors. The meetings also provided information in a more timely manner than is possible from published documents, which usually appear some time after the reported work is carried out. At each of the Technical Exchanges, some suggestions were outlined for future NRC/NBS interactions with WVDP/DWPF personnel on HLW vitrification. Technical sessions, with discussions in greater depth and sharper focus than was possible during the formal Technical Exchanges, were recommended as an effective means of keeping abreast of current developments. To date, no such meetings have been scheduled.

## 6.0 MCC -- MATERIALS CHARACTERIZATION CENTER

The Materials Characterization Center (MCC) was established by the Department of Energy (DOE) in 1980 to ensure that qualified materials data are available on nuclear waste materials. This purpose is being met by (1) developing standard test methods and having them approved, (2) testing nuclear waste materials using approved test methods, and (3) publishing test procedures and data in the Nuclear Waste Materials Handbook. Test methods and data packages are submitted to the Materials Review Board (MRB) for approval. Organizationally, the MCC and the MRB are under the Materials Integration Office (MIO) which is based in Chicago, Illinois. The MRB is made up of individual scientists from government and academia. The MCC is located in Richland, Washington and is operated for the DOE by the Pacific Northwest Laboratories (PNL) of the Battelle Memorial Research Institute. The MCC is supported at approximately a sixty percent level by the DOE; the remainder of MCC's funding comes from other DOE offices dealing with repositories and other aspects of nuclear waste materials. The MCC prepares monthly reports in addition to project reports and other various reports submitted to its supporting agencies.

The MCC monthly reports are divided into the following categories.

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

This report is a brief summary of MCC activities from January 1, 1987 through June 30, 1987. The reader is referred to the monthly reports for further details or for information not discussed here.

## 6.1 Program Administration

The organization of the MCC stayed essentially the same as that reported earlier, in Figure 1 of NUREG/CR-4735, Vol. 2, 1987, page 18 [Interrante, 1987b]. Work was initiated for the Sandia National Laboratory, and this is reported in the Transportation Technology Section of this report. The MCC manager attended a program review at West Valley, New York and also met with Materials Integration Office (MIO) manager in Chicago, Illinois to discuss the status of the MCC. There were other reviews, planning meetings and submission of statements of work (SOW) and plans carried out under program administration. There was a midyear review of the MCC status in terms of budget, schedule, milestones and open issues held in May 1987. Also the manager of MIO and technical support staff from Argonne National Laboratory (ANL) visited PNL in May to discuss an MCC five-year plan and the 1988 program. No information pertaining to the findings of the review or the meeting was given.

## 6.2 Quality Assurance

Records were collected for all tasks and transferred to the PNL Record Center. SRP and also BWIP records were reviewed and turned over to the respective projects. Records for reference glasses, ATM-5, ATM-6, ATM-3, ATM-4, ATM-1 and MCC-76-68 were transferred to the PNL Record Center for life-time storage. Plans were started for archival storage of ATM-5 and ATM-6 reference glasses. Storage must meet requirements of PAP-802, Test Material and Sample Archiving and also the more stringent requirements of the Nuclear Materials Inventory.

The MCC Quality Assurance Plan, WTC-002, reflects the formation of the Waste Technology Center (WTC) and incorporates SRP, BWIP and WVDP.

An internal PNL Quality Assurance (QA) audit was conducted in April 1987 and corrections were made regarding findings and observations. Various other audits were held during the six-months covered in this report, and corrections were made. There is increased emphasis on QA, including areas of procedures, reviews, staff credentials and training.

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

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

The ASTM interactions are with Committee C26 on Nuclear Waste Materials. The ASTM activity on drafting a practice for accelerated testing was completed, and no further activity is planned and no further OGR support has been allocated. The MCC-1 Static Leach Test was balloted through the ASTM, and a combined subcommittee/committee ballot was sent out in June and should have been completed by July 1987.

The Spent Fuel Working Group (SFWG) met in January 1987 to review a draft list of spent fuel characteristics. Radiochemical testing is being conducted to determine fission gases including $^{129}I$ on the cladding and $^{135}Cs$ in the fuel.

Metallography/Ceramography and transmission electron microscopy (TEM) are being used for solid state analysis. Gamma scans of ATM-106 fuel rods showed high fission-gas release for some rods, but not for all, and this is being studied. Gamma scans of ATM-105 (BWR) showed higher activity in the bottom half of the fuel rod, and duplicate runs were made to verify this finding.

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

## 6.4 Salt Repository Project

This activity deals with a number of topics including test method development, workshops such as one held on stress corrosion cracking, sensing electrodes, and stability of brines. A draft was prepared on "Validation of Corrosion Tests." This involves test procedures for container materials under anticipated salt repository conditions. Additional material was incorporated in the SRP-BNL 1 Standard Test Method for Salt Irradiation Testing, and this method was submitted to the Lawrence Berkeley Laboratory for external peer review. The SRP-WPP 18 corrosion test method entitled "New Standard Test Method for Determination of General Corrosion Rate of Candidate Structural Materials in Brines and Brine/Salt Mixtures" was balloted through the ASTM C26.07 task group. Three negative votes were received. Plans are to eventually submit SRP-WPP 18 for ballot at the subcommittee level.

Development of a pH sensing electrode and of pH and Eh reference electrodes continued, and tests for this development and for calibration were conducted. Efforts are being made to correct for sources of uncertainty in measuring hydrogen-ion activity, and the MCC investigators are interacting with the PNL waste-package program investigators in activities relevant to other salt repository studies. Laboratory tests are being conducted to determine the compositional stability of brines.

## 6.5 Basalt Waste Isolation Project

All experimental work in this activity was stopped in November 1986, and records were transmitted to the Record Center. Work on the Development of the MCC/BWIP 14.4 Waste Form Compliance Test Method has continued. This test deals with leach rates of glass waste forms such as ATM-10 and ATM-11. Hot testing of ATM-11 has been delayed awaiting BWIP concurrence and the setting up of appropriate test facilities.

## 6.5 Defense High-level Waste Technology Project

This activity involves test method standardization, reference and testing materials, a database, waste form durability, canister materials performance, models and thermal and processing properties. The MCC-3 Agitated Powder Leach Test Method was submitted to the MRB, with changes essentially the same as those made in MCC-1.

Leach testing was completed on saw-cut round-robin specimens, cut by five different laboratories using a standard procedure, to determine if there were significant differences in leaching. Data were incorporated into MCC-1 Static Leach Test Procedure and the procedure was resubmitted to the MRB.

There are 597 papers in the glass thermal property database, and 370 of these are on borosilicate glass. There are approximately 400 papers either received or on order on glass durability. A comparison of this database activity with the National Bureau of Standards (NBS)/Nuclear Regulatory Commission (NRC) indicated that the NBS/NRC database was a highly refined literature search that tells where the data is but does not contain any tabulations of data. This is true, the NBS database is actually a data index, and the user of the NBS/NRC database must obtain the data from the referenced papers. The NBS/NRC database does give lists of all data available in a document; in addition, it gives a technical evaluation of the data and its relevance to issues dealing with nuclear-waste storage.

No funding was provided for the fabrication of ATM-18.

## 6.6 Transportation Technology Center

At the beginning of this reporting period in January 1987 insufficient funding was available for the TTC work. Funds were approved in April. A Transportation Flaw Leak Test was developed. This test uses nucleopore filters for collecting fine glass which exits flaws during a 2000 mile transport. Related work was conducted on the development of a Pressurized Flaw Leak Procedure. Part of the reason for developing and conducting these tests is to determine if any amount of respirable fines and glass material are released. Flaw leak testing was conducted on glass filled canisters which were transported from the Hanford Site to Cheyenne, Wyoming, and back to the Hanford Site, a distance of approximately 2000 miles. After the trip, filters and collected glass were removed and amounts released were correlated with the reference design flaw and its position on the canister. Size distribution of the fines were shown for each filter number (reference design flaw). Data from these tests do not take into account effects on the glass of aging, decay heating or irradiation.

## 6.7 West Valley Demonstration Project

This activity deals with reference glass durability testing, characterization and documentation of some Approved Test Materials (ATMs), fabrication of some ATMs and a database. All reference glass tests are in progress or have been completed. MCC-1 and MCC-3 leach tests of ATM-10, CTS glass and ARM-1 in deionized water and MCC-1 tests of CTS glass in PBB-1 brines were completed and summarized in a report, and forwarded to the WVDP. This report, also contains a statistical analysis of the results. The conclusion given in the report was that the leaching behavior of the West Valley glass was comparable to that of the other waste glasses tested and that the West Valley glass met the NNWSI criterion of leaching losses for specified elements of less that 1 $g/m_2$ per day averaged over the first 28 days. Earlier reports stated that the ATM-10 was more durable than the CTS glass. Pulsed flow tests of CTS glass, ATM-10, and ARM-1 were completed. Initially the leach-release-rate from the CTS glass was approximately four times greater than that of ATM-10 glass. Later, the leach rate of CTS glass decreased due to the slow transport of silicic acid in the growing surface layer on the glass particles. This decrease in leach rate is not observed in the more durable glasses.

Characterization of ATM-10 and a statistical analysis of the ATM-10 composition data were completed. The ATM-10 materials were packaged and sent for use by the West Valley test program at PNL, the Nevada Nuclear Waste Storage Investigations (NNWSI) program at the Lawrence Livermore National Laboratory (LLNL), and the Salt Repository Laboratory (SRL). Fabrication of the nonradioactive ATM-WV/205 reference glass, containing dopants, was completed, and characterization of ATM-WV/205 is nearing completion.

An Analytical Methods Workshop was held in April 21-22, 1987 at the Battelle Seattle Research Center. This workshop was supported by WVDP, OGR and DHLWTP. There were about 15 participants from six DOE and contractor laboratories in addition to two NBS scientists specializing in sample preparation methods and analyses by inductively coupled plasma (ICP) and x-ray fluorescence (XRF).

Work is continuing on setting up a computerized system for the database. This is a multifunded task, supported at present, by the WVDP and the DHLWTP. The purpose of this database is to compile the material properties data that is needed by nuclear waste glass producers, the repositories and other participants in the waste licensing process. The outline for the database handbook is as follows.

COMPREHENSIVE DATABASE HANDBOOK

I. INTRODUCTION
II. SCOPE
III. CONVERSION CONSTANTS, SYMBOLS, etc.
IV. GLASS WASTE FORM PROPERTIES
   A. LEACHING, DISSOLUTION PERFORMANCE
   B. THERMAL STABILITY UNDER PROJECTED TEMPERATURES
   C. THERMAL and PROCESSING PROPERTIES
   D. REACTIVITY/CHEMICAL COMPATIBILITY with CANISTER/FILLER
   E. BULK PHYSICAL PROPERTIES

Comments - The monthly reports of the MCC indicate that the center is responsive to the offices that support it. There is considerable effort spent on quality assurance as indicated by various audits and reviews and corrections made. During this reporting period, there was progress made in developing, testing and characterizing some of the ATM waste glasses. Most of the work done at the MCC is supported by the OGR, SRP, DHLWTP, TTC, WVDP and to a lesser extent, BWIP. There is essentially very little work done for the NNWSI.

It is not clear why there is not more support for the development of standard approved-test methods. Other standards groups, such as the various ASTM committees and the NBS, have demonstrated that the time invested in developing test procedures, material specifications, etc. produces useful results. The approval process through the MRB is not unreasonable, as evidenced by the development of some of the more difficult and complex leach tests that have or are nearing final approval. The additional step of getting input from various ASTM committee memberships is helpful, but the MCC has the final responsibility to determine the test methods and materials specifications that will be submitted to the MRB for approval and use.

The activity of working with ASTM Committee C26 to develop a document for accelerated testing had been in progress for about one year. Support for this effort has been discontinued by the OGR. The accelerated testing activity needed input and cooperation of the repositories, and this input had been requested in the previous six month reporting period [Interrante, 1987b]. No information regarding the contents of the final accelerated testing document or reasons for not continuing this work were given in the MCC reports.

## 7.0 AN ILLUSTRATION OF UNCERTAINTIES IN THE CHOICE OF GLASS COMPOSITION

An illustration of the importance of interpretation of data is given so as to stress the need for independent interpretation of data to be used to predict the performance of materials proposed for use in a nuclear waste package. This illustration contrasts published (Chick, et al. 1984) results with substantially different results obtained from an alternate NBS interpretation of these data.

The example used in this illustration involves a response surface model of the type that will be used for waste package decisions. Glass compositions for the vitrification of high-level nuclear waste are being chosen, in part, on the basis of empirical models of performance characteristics such as leaching. These models are response surface models. They describe a relation between glass performance and controlled variables that affect performance. The performance parameters in question are the leaching characteristics of the glass. Pertinent controlled variables are the glass composition and the processing (melting/cooling) conditions used in the production of the glass.

The NBS analysis assumed that glass containing greater than 25% $Na_2O$ have leach rates that are so high that these glasses are undesirable. Further, the higher compositions would complicate the analysis and the model needed to portray the data. Thus, the NBS analysis is not applicable to glass above the 25% level for $Na_2O$. A conclusion reached from this alternate analysis is that leach rates of glass recommended in the original report would be improved by changing the recommended composition, in particular, by substitution of $Al_2O_3$ for $Na_2O$ -- it is noted that there must be a trade of between leachability and producibility of borosilicate glass, and that the suggested addition of the alumina may be unwarranted when all factors are considered. Nevertheless, alternate interpretations of these data have led to alternative recommendations for the composition of glass for this application. Hence, the example serves its intended purpose of illustrating the benefit and necessity of independent interpretation of data taken to represent materials performance.

Empirical models entail a variety of uncertainties that must be assessed before conclusions are finalized. The uncertainties that are most difficult to assess are those connected with the choice of a parametric form for the model. Resolution of questions of the proper choice of the form of the model is the subject of this section.

The response-surface models that relate glass performance to the various controllable variables typically involve polynomials in the controllable variables. Generally, a separate model is developed for each performance characteristic, which in the case of glass leaching means a separate model for each component measured in the leachate. Let y denote a performance characteristic, and let x, z, ..., denote the controllable variables. The variable y might be the normalized concentration of $SiO_2$ in the leachate or the logarithm of this normalized concentration, and x and z might be the proportion of $SiO_2$ and $B_2O_3$ in the glass, for example. Response surface models typically have the form

$$y = \beta_0 + \beta_1 x + \beta_2 z + \beta_3 xz + \beta_4 x^2 + \beta_5 z^2 + \ldots,$$

where, of course, the number of controllable variables might be larger than two and the polynomial on the right side might be of higher order than quadratic. One important characteristic of a model of this form is that it can represent a performance characteristic that attains an optimum level for some setting of the controllable variables.

Consider the experiment needed to obtain a response surface model for a particular performance characteristic. Such an experiment is composed of trials. In each trial, the performance characteristic is measured for a particular setting of each of the controllable variables. Such an experiment entails more than the estimation of the parameters $\beta_0$, $\beta_1$, .... The experiment must also provide a basis for choosing the form of the polynomial to be used for the response surface, any transformation that is to be applied to the response variable y, and the region in the space of the controllable variables over which the response surface is valid. These latter choices involve uncertainties that are much more difficult to quantify than the uncertainty in the estimation of the parameters $\beta_0$, $\beta_1$, ....

After a response surface is determined for each of the performance characteristics of interest, the best glass composition and processing procedure are to be chosen. Moreover, tolerance limits that assure that the glass created is reasonably close to the best obtainable are also to be chosen. Since the various performance characteristics will not all reach optimum levels for same setting of the controllable variables, this choice involves tradeoffs. This section will not discuss these tradeoffs. The purpose of this section is to discuss the response surfaces that must be estimated in preparation for making the tradeoffs.

As an example of the uncertainty associated with the choice of the form of the model, we consider the study by Chick, et al. When this study was conceived, the designers thought that quadratic response surface models would be adequate for the region containing the glass compositions of interest. Thus, the response surface experiment was designed to provide precise estimates of the coefficients of quadratic models [Chick, 1984]. Unfortunately, a quadratic model was not adequate for any of the performance characteristics considered. Thus, as part of the data analysis, a decision had to be made about how to obtain adequate models. This decision introduces an uncertainty into the modeling that is not reflected in the usual standard errors of the parameters $\beta_0$, $\beta_1$, .... These authors decided to fit a cubic response surface model as a solution to their modeling problem. This solution is not the only alternative.

In the fitting of empirical models, the investigator can choose between fitting a simpler model to a smaller region or fitting a more complicated model to a larger region. The authors of this study chose the latter alternative. Inspection of the data suggests that the reason that a quadratic model does not fit is that the region over which the experimental points are spread includes concentrations of $Na_2O$ that are too high, as indicated by high rates of leaching at the external of the available data. Thus, an alternative to a cubic model is a quadratic model over a smaller region. A smaller region that seems to allow an adequate fit to a quadratic model has an upper bound on $Na_2O$ of 0.25 instead of the original upper bound of 0.30. This restriction eliminates 25 of the 101 original data points. It also simplifies the model by eliminating 35 terms. The fits of the two models can be compared on the basis of the residuals for the data points with $Na_2O$ less than 0.25. On this basis, the alternative quadratic model seems to fit nearly as well as the original cubic model.

Our comparison of the two models is based on the contour plots shown in Figures 1-4. Before discussing the comparison, we consider the interpretation of these plots. Consider the top plot in Figure 1. This plot shows the logarithm of the normalized Si release for the 28-day MCC-1 test as a function of the seven components that make up the glass [Chick, 1984]. Of the seven components, three are allowed to vary in each of these contour plots and the other four are held constant at the proportions for the glass recommended as optimum in the study, $SiO_2$ 0.454, $B_2O_3$ 0.024, $Na_2O$ 0.155, CaO 0.102, $Al_2O_3$ 0.009, $Fe_2O_3$ 0.135, and Waste 0.121. The level of the response is shown by the letters, and a scale for the letters is shown on the right of the plot. Note that the B's in the middle of the plot indicate a minimum in the Si release. In the plot on top of Figure 1, the response is shown as a function of $Al_2O_3$, $Na_2O$, and Waste. These three components must add to 0.285 since the other four components are fixed. The component $Al_2O_3$ is constant along horizontal lines, lines parallel to the base of the triangle. The component $Na_2O$ is constant along lines parallel to the left side of the triangle. The component Waste is constant along lines parallel to the right side of the triangle. The minimum shown by the B's is near the proportions $Al_2O_3$ 0.09, $Na_2O$ 0.155, and Waste 0.04. Thus, this Figure suggests that better leach performance can be obtained by substituting $Al_2O_3$ for Waste.

The two contour plots in Figure 1 contrast the original cubic model shown on the top with the alternative quadratic model shown on the bottom. The two plots are generally similar. However, the quadratic model does not show a distinct minimum in the middle as the cubic model does. Rather, the quadratic model suggests that better leach performance can be obtained by substituting $Al_2O_3$ for $Na_2O$ while holding the waste proportion constant.

Figure 2 also contrasts the cubic and quadratic models but in terms of a different perspective on the response surface. The study by Chick, et al. discusses the fact that better leach performance can be obtained with more CaO and less $B_2O_3$ than has been recommended in previous studies [Chick, 1984]. While this conclusion seems to generally hold for both models, the change in leach behavior is more gradual under the quadratic model. Moreover, the quadratic model shows a minimum at the lowest level of $Na_2O$ for $B_2O_3$ near 0.06.

Figure 3 shows the quadratic model obtained for another leach component, the logarithm of the normalized Waste from the 28-day MCC-1 test. The top plot shows the same components as Figure 1, and the bottom plot shows the same components as Figure 2. The top plot shows distinctly that better leach performance can be obtained by substituting $Al_2O_3$ for $Na_2O$ while holding the Waste constant. The bottom plot supports the assertion in the original study that better performance is obtained with higher CaO and correspondingly lower $B_2O_3$.

Figure 4 shows the quadratic model obtained from the composite leach measure used in the original study to judge leach performance. Again the top plot corresponds to Figure 1, and the bottom to Figure 2. The top plot shows better leach performance is obtained with more $Al_2O_3$ and less $Na_2O$. The bottom plot suggests that for low levels of $Na_2O$, the substitution of CaO for $B_2O_3$ can be carried too far.

Can one of the two alternative models be selected on the basis of the data available? In this study, the selection of one of these models is hampered by the fact that too few replicate data points were obtained. Only ten replicates were run, and of these one pair of results was eliminated because of mistakes in the laboratory work. Without an adequate assessment of the pure error in an experiment, the choice between alternative models is difficult.

The above example discusses the choice between two alternative models with attendant alternative regions of validity. Besides the choice of model complexity and region of interest, there is the choice of transformation of the response variable. In the above example a log transform was chosen. Although this is a reasonable choice, alternatives might be proposed that cannot be eliminated on the basis of the available data.

Consider the uncertainties associated with the choice of model complexity, region of validity, and response-variable transformation. In the choice of the composition of the nuclear waste glasses, these uncertainties must be treated in an objective manner. But how is this to be done? There is no standard method for describing the uncertainties associated with these choices as there is for describing the uncertainties in the parameters $\beta_0$, $\beta_1$, .... The statistics literature contains some methods for making these choices, which are applicable if the proper set of trials have been run. The literature suggests methods for characterizing the associated uncertainties but these methods are neither simple nor standard.

In the study discussed above, the authors defend their choice of a cubic model in two ways. First, they eliminated terms from the full cubic model by stepwise regression. Then they argue that since the number of independent terms in the model is much smaller than the number of different trials, the available data provides adequate estimates for the coefficients in their model. Second, they argue that their model is adequate because its $R^2$ is high. Although too many parameters for the number of data points or a small value of $R^2$ indicate a modeling problem, the converse is not true. In particular, neither of their arguments rules out the quadratic alternative suggested above.

A solution to the problem of the uncertainties associated with the choice of model form is reanalysis of the data by an independent investigator. This solution, which is widely recognized in science, requires that the investigators responsible for the initial recommendations on glass composition make all their data available to others, as the authors of the study discussed above did. An independent investigator should be provided a machine-readable file containing the valid measurements, the results of the measurement assurance program from the laboratory that performed the work, and a discussion of any outliers suspected by the original investigators. A reanalysis requires time and money, which must be provided at the planning stage.

A reanalysis of the data will raise questions about the initial analysis but is unlikely to resolve these questions. Resolution of the questions will undoubtedly require additional experimental work. The additional experimental work might include trials for glass compositions closer to the recommended composition or trials that would allow a more complicated model to be fit and compared to the initial model.

The confirmatory experiment should, of course, be built on the initial experiment. This does not mean that the confirmatory experiment will be smaller than the initial experiment. Further experimentation associated with the example discussed above might require the measurement of as many different glass compositions as considered originally. The questions to be answered in the confirmatory experiment might be difficult to answer because of the experimental error and thus might require a large number of trials for resolution.

In the response surface literature, confirmatory experiments are almost universally recommended although one might suspect that they are less than universally performed. The choice of composition for the nuclear waste glasses is certainly critical enough to warrant a confirmatory experiment by an independent organization.

Confirmatory experiments are not inexpensive. However, the effort spent struggling with inadequate data is also very expensive given all costs are properly considered. For example, an explanation to a lay audience of why a decision was made despite inadequate data can take an enormous amount of preparation. A confirmatory experiment that reaches essentially the same conclusion as the initial experiment will usually be accepted as conclusive by the scientific community.

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                     ECHIP                               Si_28DAY
                0.00 *.* 0.22
                     /EEE\                               A = 0.0000
                    /E,,,,\                              . = 0.2308
                   /,,,DDDD\                             B = 0.4615
                  /DDDDD....\                            , = 0.6923
            0.05 *DD.......CC* 0.16                      C = 0.9231
      e          /.....CCCCCCCC\           A             . = 1.1538
     t          /..CCCCCCCC,,,,,\           1            D = 1.3846
    s          /CCCCCC,,,,,,,,,,,\           2           , = 1.6154
   a          /CCCC,,,,,,,,,,,,,,,\           O          E = 1.8462
  W  0.11    *CCC,,,,,,,,,,,,,,,,,,* 0.11     3          . = 2.0769
            /CC,,,,,,,,,BBBBBB,,,,,,\                    F = 2.3077
           /C,,,,,,,,,,BBBBBB,,,,,,,,\                   , = 2.5385
          /C,,,,,,,,,,,,,,,,,,,,,,,,,,\                  G = 2.7692
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      /CCCCCCCCCCCCCCCCCCCCCCCC........DDD\              B2O3 = 0.024
     /CCCCCCCCCCCCCCCCC..........DDDDDDD,,,\             CaO = 0.102
    /CCCCC................DDDDDDDD,,,,,,EEEE\            Fe2O3 = 0.135
0.22 *............DDDDDDDDDD,,,,,,,,EEEEEE.....* 0.00
     **---------*---------*---------*---------**
   0.07      0.12      0.18      0.23      0.28
                       Na2O
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                0.00 *,* 0.22
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            0.05 *CCCCCCCCCCC* 0.16                      C = 0.9231
      e          /CCCCCCCCCCCCC\           A             . = 1.1538
     t          /CCCCCCCCCCCCCCC\           1            D = 1.3846
    s          /CCCCCCCC,,,,,,,,,\           2           , = 1.6154
   a          /,,,,,,,,,,,,,,,,,,,\           O          E = 1.8462
  W  0.11    *,,,,,,,,,,,,,,,,,,,,,* 0.11     3          . = 2.0769
            /,,,,,,,,,,,,,,,,,,,,,,,\                    F = 2.3077
           /,,,,,,,,,,,,,,,,,,,,,,,,,\                   , = 2.5385
          /,,,,,,,,,,,,,,,,,,,,,,,,,,,\                  G = 2.7692
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   0.16 *,,,,,,,,,,,,,CCCCCCCCCCCCCCCCCC* 0.05
       /,,,,,,,CCCCCCCCCCCCCCCCCCCCCCCCCC\               SiO2 = 0.454
      /,CCCCCCCCCCCCCCCCCCCCCCCCCC........\              B2O3 = 0.024
     /CCCCCCCCCCCCCCCCC....................\             CaO = 0.102
    /CCCCCCCCCCC.....................DDDDDDD\            Fe2O3 = 0.135
0.22 *CCCC...................DDDDDDDDDDDDDDDDD,* 0.00
     **---------*---------*---------*---------**
   0.07      0.12      0.18      0.23      0.28
                       Na2O
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Figure 1. Normalized Si Release (Chick, et al. 1984) predicted by cubic model from 101 data points (TOP) and quadratic model from 76 data points (BOTTOM).

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                 ECHIP
             0.00 *E* 0.28
                  /,,,\
                 /,,,,,\
                /,,,,,,,\
               /DD,,,DDDD\
     0.05 *DDDDDDDDDDD* 0.23
             /DDDDDDDDDDDDD\          N
  O         /DDDDDDDDDDDDDDD\          a
 a         /.DDDDDDDDDDDDDDDD\          2
C         /...DDDDDDDDDDDDDDDD\          O
   0.11 *.....DDDDDDDDDDDDDDDD* 0.18
        /.......DDDDDDDDDDDDDDDD\
       /........DDDDDDDDDDDDDDDDD\
      /C........DDDDDDDDDDDDDDDDDD\
     /CC........DDDDDDDDDDDDDDDDDDD\
0.16 *CCC......DDDDDDDDDDDD,,,,,,,,,,* 0.12
    /CCCC......DDDDDDDDDD,,,,,,,,,,,,,\
   /CCCCC......DDDDDDDD,,,,,,,,,,,,,,,,\
  /CCCCCC.....DDDDDDDD,,,,,,,,,,,,EEEEEE\
 /CCCCCC.......DDDDDDD,,,,,,,,,EEEEEEEEEE\
0.21 *,CCCCCC.....DDDDDDD,,,,,,,EEEEEEEEE....* 0.07
     **---------*---------*---------*---------**
     0.00      0.05      0.11      0.16      0.21
                         B2O3
```

Si_28DAY

A = 0.0000
. = 0.2308
B = 0.4615
, = 0.6923
C = 0.9231
. = 1.1538
D = 1.3846
, = 1.6154
E = 1.8462
. = 2.0769
F = 2.3077
, = 2.5385
G = 2.7692
. = 3.0000

SiO2 = 0.454
Al2O3 = 0.009
Fe2O3 = 0.135
Waste = 0.121

```
                 ECHIP
             0.00 *,* 0.28
                  /,,,\
                 /D,,,,\
                /DDDD,,,\
               /DDDDDD,,,\
     0.05 *DDDDDDDDD,,* 0.23
             /.DDDDDDDDDD,,\          N
  O         /....DDDDDDDDD,,\          a
 a         /......DDDDDDDDDD,\          2
C         /.........DDDDDDDDD,\          O
   0.11 *...........DDDDDDDDD,* 0.18
        /..............DDDDDDDD,\
       /................DDDDDDDD,\
      /..................DDDDDDDD,\
     /....................DDDDDDDD,\
0.16 *......................DDDDDDDD,* 0.12
    /........................DDDDDDDD,\
   /..........................DDDDDDDD,\
  /............................DDDDDDD,,\
 /..............................DDDDDDD,,\
0.21 *............CC.................DDDDDDDD,,* 0.07
     **---------*---------*---------*---------**
     0.00      0.05      0.11      0.16      0.21
                         B2O3
```

Si_28DAY

A = 0.0000
. = 0.2308
B = 0.4615
, = 0.6923
C = 0.9231
. = 1.1538
D = 1.3846
, = 1.6154
E = 1.8462
. = 2.0769
F = 2.3077
, = 2.5385
G = 2.7692
. = 3.0000

SiO2 = 0.454
Al2O3 = 0.009
Fe2O3 = 0.135
Waste = 0.121

Figure 2. Normalized Si Release (Chick, et al. 1984) predicted by cubic model from 101 data points (TOP) and quadratic model from 76 data points (BOTTOM).

```
                              ECHIP
                          0.00 *.* 0.22
                              /EEE\
                             /,,,,,\
                            /DDDDDDD\
                           /.........\
                 0.05 *CCCCCCCCCCC* 0.16
         e                /,,,,,,,,,,,,,\              A
        t                /BBBBBBB,,,,,,,,\              l
       s                /BBBBBBBBBBBBBBBBB\              2
      a                /.........BBBBBBBBBB\              O
     W   0.11 *..............BBBBBBB* 0.11   3
                     /AAAAA............BBBBBB\
                    /AAAAAAA............BBBBBB\
                   /AAAAAAAA...........BBBBBBBB\
                  /AAAAAAAA...........BBBBBBBBBB\
        0.16 *AAAAAAA..........BBBBBBBBBB,,,,* 0.05
                /AAAAA..........BBBBBBBBB,,,,,,,,,\
               /AA..........BBBBBBBBB,,,,,,,,CCCCCC\
              /........BBBBBBBBB,,,,,,,,CCCCCCCC....\
             /....BBBBBBBB,,,,,,,,CCCCCCCC........DDD\
       0.22 *BBBBBBB,,,,,,,,CCCCCCCC.......DDDDDDD,,,,* 0.00
            **---------*---------*---------*---------**
          0.07      0.12      0.18      0.23      0.28
                              Na2O
```

Waste_28

A = -1.0000
. = -0.7155
B = -0.4309
, = -0.1464
C = 0.1381
. = 0.4227
D = 0.7072
, = 0.9918
E = 1.2763
. = 1.5608
F = 1.8454
, = 2.1299
G = 2.4144
. = 2.6990

SiO2 = 0.454
B2O3 = 0.024
CaO = 0.102
Fe2O3 = 0.135

```
                              ECHIP
                          0.00 *F* 0.28
                              /...\
                             /EEE..\
                            /,,EEEEE\
                           /D,,,,,EEE\
                 0.05 *DDDDD,,,,EE* 0.23
                         /...DDDDD,,,,E\            N
         O              /.......DDDD,,,,\            a
        a              /CCCC......DDDD,,,\            2
       C              /CCCCCCC......DDDD,,\            O
          0.11 *,,CCCCCCCC.....DDDD,,* 0.18
                    /,,,,,,CCCCCCC.....DDD,,\
                   /,,,,,,,,,CCCCCC.....DDD,,\
                  /,,,,,,,,,,,,CCCCCC....DDD,,\
                 /,,,,,,,,,,,,,,CCCCCC....DDD,,\
        0.16 *,,,,,,,,,,,,,,,,CCCCC....DDDD,,* 0.12
               /,,,,,,,,,,,,,,,,,CCCCCC....DDD,,,\
              /,,,,,,,,,,,,,,,,,,,CCCCC....DDDD,,,\
             /,,,,,,,,,,,,,,,,,,,,CCCCCC....DDD,,,E\
            /,,,,,,,,,,,,,,,,,,,,,CCCCCC....DDD,,,EE\
      0.21 *C,,,,,,,,,,,,,,,,,,,,CCCCCC.....DDD,,,,EE* 0.07
           **---------*---------*---------*---------**
          0.00      0.05      0.11      0.16      0.21
                              B2O3
```

Waste_28

A = -1.0000
. = -0.7155
B = -0.4309
, = -0.1464
C = 0.1381
. = 0.4227
D = 0.7072
, = 0.9918
E = 1.2763
. = 1.5608
F = 1.8454
, = 2.1299
G = 2.4144
. = 2.6990

SiO2 = 0.454
Al2O3 = 0.009
Fe2O3 = 0.135
Waste = 0.121

Figure 3. Normalized Waste Release (Chick, et al. 1984) predicted by quadratic model from 76 data points.

```
                 ECHIP                                      SI4PH_Composite
              0.00 *.* 0.22
                  /...\                                     A =  1.000
                 /.....\                                    . =  1.692
                /.CCCCCC\                                   B =  2.385
               /CCCCCCCCC\                                  , =  3.077
         0.05 *CCCCCCCCCCC* 0.16                            C =  3.769
     e       /CCCCCCCCCCCCC\       A                        . =  4.462
    t       /CCCCCCCCCCCCCCC\       l                       D =  5.154
   s       /CCCCCCCCCCCCCCCCC\       2                      , =  5.846
  a       /CCCCCCCCCCCCCCCCCCC\       O                     E =  6.538
 W  0.11 *,CCCCCCCCCCCCCCCCCCCC* 0.11  3                    . =  7.231
         /,,,CCCCCCCCCCCCCCCCCCCC\                          F =  7.923
        /,,,,CCCCCCCCCCCCCCCCCCCCC\                         , =  8.615
       /,,,,,CCCCCCCCCCCCCCCCCCCCCC\                        G =  9.308
      /,,,,,CCCCCCCCCCCCCCCCCCCCCC..\                       . = 10.000
 0.16 *,,,,,CCCCCCCCCCCCCCCCCC........* 0.05
     /,,,,CCCCCCCCCCCCCCCC.............\                    SiO2 = 0.454
    /,,,,CCCCCCCCCCCCC.................D\                   B2O3 = 0.024
   /,,,CCCCCCCCCCCC..............DDDDDDD\                   CaO = 0.102
  /,,,CCCCCCCCCC............DDDDDDDDDDDDDD\                 Fe2O3 = 0.135
0.22 *,,CCCCCCCCCC..........DDDDDDDDDDDDD,,,,,,* 0.00
     **---------*---------*---------*---------**
  0.07      0.12      0.18      0.23      0.28
                       Na2O
```

```
                 ECHIP                                      SI4PH_Composite
              0.00 *,* 0.28
                  /,,,\                                     A =  1.000
                 /D,,,,\                                    . =  1.692
                /DDD,,,,\                                   B =  2.385
               /DDDDD,,,,\                                  , =  3.077
         0.05 *DDDDDDDD,,,* 0.23                            C =  3.769
             /.DDDDDDDDD,,,\            N                   . =  4.462
   O        /...DDDDDDDDDD,,\            a                  D =  5.154
  a        /......DDDDDDDDD,,\            2                 , =  5.846
 C        /........DDDDDDDDDD,\            O                E =  6.538
    0.11 *...........DDDDDDDDDD* 0.18                       . =  7.231
        /..............DDDDDDDDD\                           F =  7.923
       /................DDDDDDDD\                           , =  8.615
      /..................DDDDDDD\                           G =  9.308
     /....................DDDDDD\                           . = 10.000
 0.16 *.......................DDDDD* 0.12
     /...........................DDD\                       SiO2 = 0.454
    /.............................DD\                       Al2O3 = 0.009
   /...........CCCCCC.................\                     Fe2O3 = 0.135
  /.........CCCCCCCCCCCCCC..............\                   Waste = 0.121
0.21 *...........CCCCCCCCCCCCCCCCCC............* 0.07
     **---------*---------*---------*---------**
  0.00      0.05      0.11      0.16      0.21
                       B2O3
```

Figure 4. Composite Leach Measure (Chick, et al. 1984) predicted by quadratic model from 76 data points.

## 8.0 STATUS OF CRYSTALLINE REPOSITORY PROJECT

### 8.1 Second Repository Status

Crystalline rock is the primary geologic media under consideration for the second repository, in addition to the sites that may be available from the first repository program and other sedimentary rock geologic formations not previously considered. Crystalline rock formations are located in 17 states in the north-central, northeastern, and southeastern regions of the United States. (See Figure 5 for map of United States crystalline regions.) The overall objective of the second repository program is to identify and evaluate methods, technologies, procedures, and materials related to waste isolation concepts, as well as various assessment technologies to characterize a site and predict performance. Because the Secretary of Energy has postponed site-specific activates related to the second repository, all crystalline-program activities will be studied on a non-site-specific basis. [DOE, 1987]

The latest projections on the amount of spent fuel which will require permanent disposal show that a second repository will be required to accommodate all the anticipated waste to be generated. [DOE, 1987] The Secretary of Energy has emphasized that even the lowest current projections of spent-fuel generation indicate that a second repository will still be needed. On May 28, 1986, however, the Secretary of Energy announced his conclusion that it would be prudent to postpone site-specific activities for the second repository. The Secretary's conclusion was based on a number of factors including the following: (1) declining projections of the rates at which spent fuel will be discharged from commercial nuclear power plants, (2) progress in siting the first repository and confidence in finding suitable sites among the three sites approved by the President for site characterization, (3) advantages to be gained from experience of the first repository, (4) the expectation of Congressional approval for the Monitored Retrievable Storage (MRS) facility, and (5) fiscal management and responsibilities [DOE, 1987]. Current plans for the second repository program include non-site-specific studies of potential host rocks, the development of analytical approaches to evaluate long-term performance, and a continuation of the current program of international cooperation [DOE,1987].

With Congressional approval, in 1995 DOE intends to begin a national survey of potential sites for a second repository. The proposed schedule will allow ample time to develop a second repository prior to the first repository reaching its 70,000-metric-ton capacity. The Nuclear Waste Policy Act of

1982 (NWPA) specifies the maximum amount of spent nuclear fuel that the Nuclear Regulatory Commission may allow to be emplaced in the first repository. The Act sets this figure at 70,000 metric tons of uranium. The schedule required for the second repository will depend on refined estimates of rates at which spent fuel is generated, the time needed for the first repository to reach the limit of 70,000 metric tons of uranium, and the time needed to develop the second repository. [DOE, 1987]

In recent amendments to the Mission Plan, the DOE presented a revised schedule for the first repository. The new schedule shows a five-year extension of the date for waste acceptance at the first repository, from 1998 to 2003. Delay in construction and the beginning of waste acceptance of the first repository will necessitate changes in the schedule for construction of the second repository. (See Figure 6 for a comparison of DOE's preliminary milestones for the second repository.)

Major accomplishments prior to 1985, for the crystalline repository project included completion of the region-to-area screening methodologies, published in final form in April 1985, and final regional characterization reports, issued in September 1985. These regional characterization reports contain available geologic and environmental information for the three regions being studied by the Crystalline Repository Project. These data were applied to the region-to-area screening methodology and the siting guidelines to assist in defining areas for further study. [DOE, 1986a]

In January 1986, the "Draft Area Recommendation Report for the Crystalline Repository Project: Overview" (DOE/CH-15) and the "Area Recommendation Report for the Crystalline Repository" (DOE/CH-15(1)) were issued. This series of reports narrows the scope of possible sites for recommendation for the second repository to specific areas within selected crystalline regions.

The experience of siting the first repository suggests that site-specific screening leading to the identification of potentially acceptable sites should start about 25 years before the start of waste acceptance for disposal. Thus, to have the second repository available by about 2025, site-specific studies need not start until the 1990s. If affirmative Congressional action is not taken, the DOE will review the more than 60,000 comments received on the draft area recommendation report issued in January 1986 and prepare a final area recommendation report that identifies potentially acceptable sites for subsequent field work. Delay in Congressional action has delayed the issuance of the final area recommendation report. (See Figure 7 for a schedule of the second repository program.)

The DOE feels that with a later decision on the siting of the second repository, a more appropriate scale of operations for that facility can be established. In addition, a longer period of time between the startup of the two repositories will permit the experience and knowledge gained in the development and operation of the first repository to be used for the second repository. This will provide the opportunity for potential technical refinements and cost savings [DOE, 1987].

## 8.2 International Cooperation

The major undertakings in FY 1988 involve activities necessary to develop and implement an integrated technology program and include activities drawing information from international cooperative efforts. The management of radioactive waste is an international concern, and many other countries have active programs for storage and disposal. The Office of Civilian Radioactive Waste Management (OCRWM) continues to participate in several significant international project and information exchange programs under bilateral, multilateral and international-agency agreements. The international agencies in which OCRWM participates are the International Atomic Energy Agency (IAEA), the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD), and the Commission of the European Communities (CEC). [DOE, 1986a]

The Stripa project is conducted in Sweden in cooperation with seven other countries and is coordinated by the NEA. Its purpose is to conduct repository performance experiments in granite. Phase II of this project, completed during 1986, provided significant information on the characterization of fracture zone, the hydrology and geochemistry of groundwater in granite formations, the potential for the migration of radionuclides, and the behavior of backfill materials. Phase III will validate groundwater flow and radionuclide transport models and study the use of materials for sealing shafts and boreholes. [DOE, 1986a]

OCRWM is cooperating with Canada in studies at the Underground Research Laboratory (URL). These studies are related to the disposal of waste in crystalline rock. Major areas of investigation are as follow: (1) the characterization of the rock (2) experiments in Canada's Underground Research Laboratory to determine the response of the rock to excavation, heat, and pressure (3) studies in the migration of radionuclides, waste interactions with containers and buffer materials and the effectiveness of shaft sealing (4) the development of models for predicting the performance of a repository (5) the development of techniques for site characterization and (6) assessment of the "disturbed zone," in which the rock is affected by the construction of the repository and emplacement of radioactive waste, as well as technologies for its stabilization. [DOE, 1986a] (See Figure 8 showing the subsurface facilities at the Underground Research Laboratory.)

The OCRWM is cooperating with Switzerland under a bilateral agreement on waste management signed in the spring of 1985. Since then, plans have been formulated to perform a number of activities considered beneficial to the geologic disposal program. These activities, expected to complement the work being performed at both the Stripa mine in Sweden and the Canadian URL, will focus on water flow and transport through fractured media and will take advantage of Switzerland's extensive experimental and data collection effort at the Grimsel Pass URL. The purpose of the Swiss program is to develop geotechnical and geophysical investigation techniques and to further evaluate the quality of granite as a host medium for radioactive waste disposal. [DOE, 1986a]

## 8.3 Conclusion

Both the schedule and any site-specific activities for the second repository have been delayed, nevertheless, the U.S. Department of Energy continues to cooperate with international groups (IAEA, NEA, and CEC) which are doing important research related to repositories in granite and crystalline rock formations.

REGIONS BEI[illegible] CONSIDERED FOR THE S[illegible]OND REPOSITORY

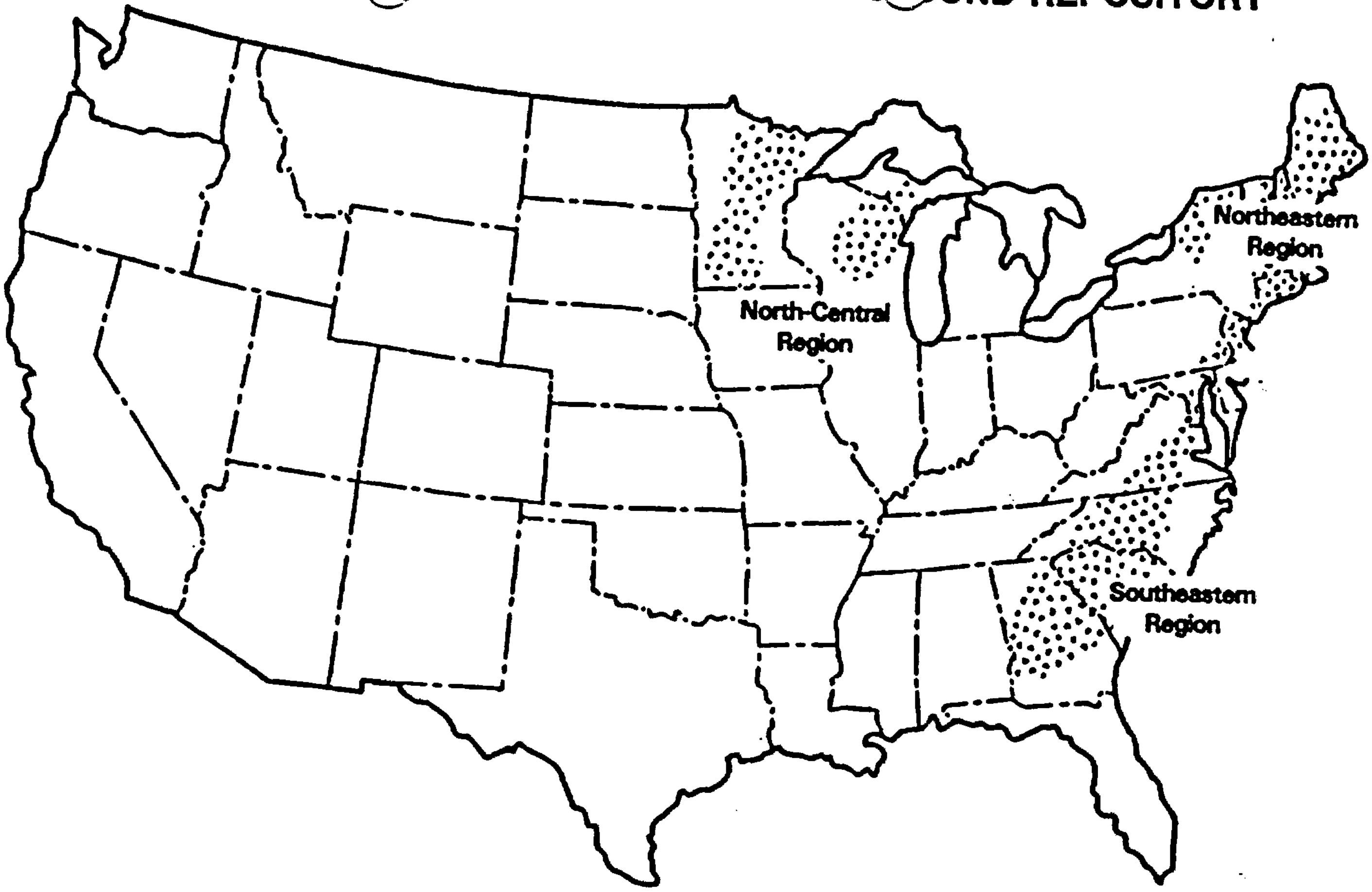


Figure 5

U.S. Department of Energy, Office Of Civilian Radioactive Waste Management, "Annual Report to Congress," DOE/RW-0004/2, March 1986.

Preliminary milestones
for two alternative second-repository programs
and comparison with the 1985 Mission Plan

| Milestone | 1985 Mission Plan | Program proposed by DOE | Alternative program if proposal is not approved by Congress |
|---|---|---|---|
| Begin national survey | 1981 | 1995[a] | (b) |
| Complete national survey | 4/83 | 1997[a] | (b) |
| Issue draft area recommendation report | 1/86 | 2000[a] | (b) |
| Issue final area recommendation report | 5/86 | 2002 | 1989 |
| Identify potentially acceptable sites | (c) | 2002 | 1989 |
| Nominate and recommend sites for characterization[d] | 10/91 | 2007 | 1994 |
| President recommends site to the Congress[e] | 1998 | 2015 | 2002 |
| Submit license application to the Nuclear Regulatory Commission | 1998 | 2015 | 2002 |
| Nuclear Regulatory Commission issues construction authorization | 2000 | 2018 | 2005 |
| Start construction | 2000 | 2018 | 2005 |
| Begin operations | 2006 | 2023 | 2010 |

[a]The program proposed by the DOE assumes that the national survey is an essentially new survey of various potential host rocks.
[b]Milestone completed.
[c]Not specified in the 1985 Mission Plan.
[d]The date mandated by the Act is July 1, 1989.
[e]The date mandated by the Act is March 31, 1990.

Figure 6

U.S. Department of Energy, Office of Civilian Radioactive Waste Management, "OCRWM Mission Plan Amendment With Comments on the Draft Amendment and Responses to the Comments," DOE/RW-0128, June 1987.

Figure 7, p. 1

SCHEDULE FOR THE CRYSTALLINE REPOSITORY PROJECT

| EVENT | COMPLETED | ANTICIPATED COMPLETION DATE |
|---|---|---|
| Nuclear Waste Policy Act Signed (P.L. 97-425) [Ref. 1, p. 5] | Jan. 7, 1983 | |
| Publication of "Response to State Comments on the Draft Regional Characterization Reports for the Crystalline Repository Project," DOE/CH-2. [Ref. 4] | Nov. 1984 | |
| Issuance of the General Guidelines for the Recommendation of Sites for the Nuclear Waste Repositories [Ref. 1, Appendix B] | Dec. 6, 1984 | |
| Publication of "Region-to-Area Screening Methodology for the Crystalline Repository Project," DOE/CH-1. [Ref. 2, p. 15] | April 1985 | |
| Publication of three response-to-state-comment documents, DOE/CH-13, DOE/CH-12, DOE/CH-14. [Ref. 2, p. 50] | Aug. 1985 | |
| Publication of three regional environmental characterization reports for North-Central, Northeastern, and Southeastern Regions, DOE/CH-5, DOE/CH-4, and DOE/CH-3. [Ref. 2, p. 16] | Sept. 1985 | |
| Publication of three regional geologic characterization reports for the North-Central, Northeastern and South-eastern Regions, DOE/CH-8, DOE/CH-7, and DOE/CH-6. [Ref. 2, p. 16] | Sept. 1985 | |
| Publication of "Draft Area Recommendation Report for the Crystalline Repository Project:Overview," DOE/CH-15, and the final "Area Recommendation Report for the Crystalline Repository," DOE/CH-15(1). [Ref. 2, p. 50] | Jan. 1986 | |

Figure 7, p. 2

| EVENT | COMPLETED | ANTICIPATED COMPLETION DATE |
|---|---|---|
| Secretary of Energy announces his decision to postpone site-specific activities for the second repository. [Ref. 3, p. 13] | May 28,1986 | |
| Issue final area recommendation report [Ref. 3, p. 15] | | 1989 |
| Identify potentially acceptable sites [Ref. 3, p. 15] | | 1989 |
| Nominate sites and recommend sites to the President for characterization [Ref. 3, p. 15] | | 1994 |
| Begin national site-screening survey of potential sites for second repository [Ref. 3, p. 54] | | 1995 |
| Completion of regional characterization reports. [Ref. 3, p. 54] | | 1999 |
| Recommend areas for more detailed study [Ref. 3, p. 54] | | 2003 |
| Beginning of field studies and identification of potentially acceptable sites. [Ref. 3, p. 54] | | 2003 |
| Recommend second repository site to Congress [Ref. 3, p. 54] | | 2007 |
| Begin operation of a second repository [Ref. 3, p. 54] | | 2023 |

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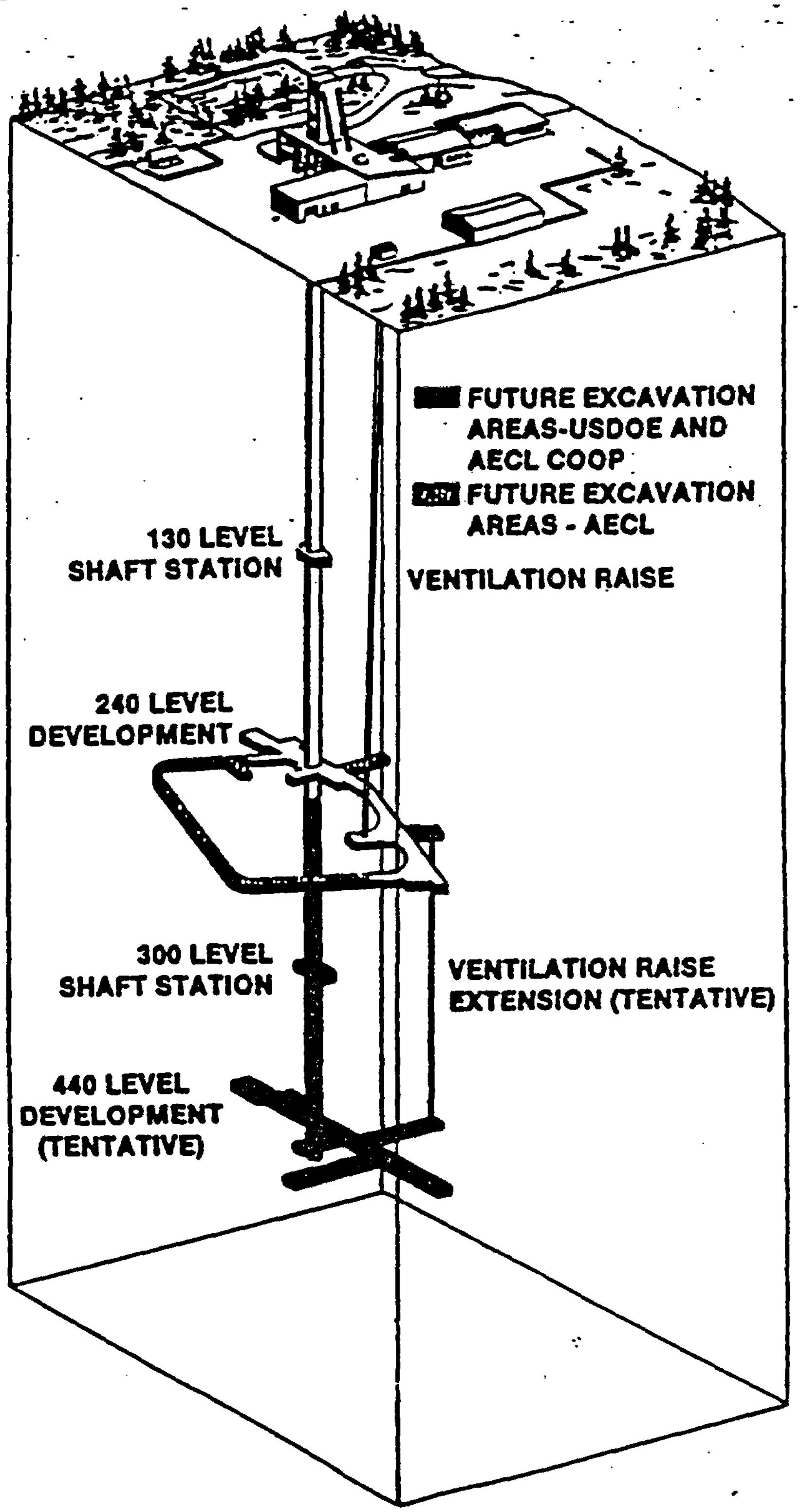
(1) U. S. Department of Energy, Office of Civilian Radioactive Waste Management, "Mission Plan for the Civilian Radioactive Waste Management Program, Volume 1," DOE/RW-0005 Vol. 1, June 1985.
(2) U. S. Department of Energy, Office of Civilian Radioactive Waste Management, "Annual Report to Congress," DOE/RW-0004/2, March 1986.
(3) U. S. Department of Energy, Office of Civilian Radioactive Waste Management, "OCRWM Mission Plan Amendment with Comments on the Draft Amendment and Responses to the Comments," DOE/RW-0128, June 1987.
(4) U. S. Department of Energy, Office of Civilian Radioactive Waste Management, "Response to State Comments on the Draft Regional Characterization Reports for the Crystalline Repository Project," DOE/CH-2, November 1984.

Existing and Future Subsurface Facilities at the Underground Research Laboratory




**CANADIAN AECL URL**

Figure 8

U.S. Department of Energy, Office of Civilian Radioactive Waste Management, "Annual Report to Congress," DOE/RW-0144, April 1987.

## 9.0 ACKNOWLEDGEMENTS

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U. S. Department of Energy, Office of Civilian Radioactive Waste Management, "Environmental Assessment, Yucca Mountain Site, Vol. 1, May 1986b.

U. S. Department of Energy, Office of Civilian Radioactive Waste Management, "OCRWM Mission Plan Amendment with Comments on the Draft Amendment and Responses to the Comments," DOE/RW-0128, June 1987.

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

Westerman, R. E. , J. H. Haberman, S. G. Pitman, and J. S. Perrin, "Corrosion of Iron-Base Waste Package Container Materials in Salt Environment," Pacific Northwest Laboratories, PNL-SA-14029, March 1986.

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

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

SRP -- SALT REPOSITORY PROJECT



VITRIFICATION OF HIGH-LEVEL WASTE

## Waste Package Data Review Form Guidelines

DATA SOURCE

Full document reference. This section will be completed for the reviewer before he/she receives the document.

DATE REVIEWED

The date the document review was completed.

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 (and/or component part, if specifically addressed as such; e.g., the screw-on type cap on a waste cylinder): e.g., 304L Stainless Steel, Brass, Zircaloy Cladding, Welds in 316 Stainless Steel, Packing Material, Basalt.

TEST CONDITIONS

(1) the State of the material being tested:
e.g., Cold Worked or Annealled 304L Stainless Steel, Thermo-mechanical History of the material (or component) studied

(2) Specimen Preparation:
e.g., 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

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

Includes the number of tables and graphs of data together with their titles and axes (indicating the range in values), e.g.:

5 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, e.g.:

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

Includes statements by the author on the applicability of the data, e.g.:

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

KEY WORDS

These are to be checked off on the keyword checklist. In general, these keywords should reflect the information given in the above categories. Additional keywords, which are truly different from terms on this list, should be added to the list as necessary.

GENERAL COMMENTS

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 would also be in this section that the reviewer would put any of his comments on the deficiencies and uncertainties in the data and analysis. e.g.:

This is a very comprehensive review of the literature on the temperature sensitization of stainless steels. Even though it neglects the definitive work of Bertocci, Shull, Kaufman, and Escalante [Phys. Rev. J13, (1879), pp. 15-358] in this area (presumably because of the difficulty in locating this document), this review still considers a sufficiently large number of other investigations to provide a good understanding of the present status of the field. The one discordant note here, however, is that it would have been a much more useful review if stainless steel types 301, 303, 304, 316, and 440C had also been addressed.

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).

## WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Argonne National Laboratory, Chemical Technology, Division, 9700 South Cass Avenue, Argonne, Illinois 60439

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

Abrajano, T., Bates, J., Ebert, W., and Gerding, T., "The Effect of Gamma Radiation on Groundwater Chemistry and Glass Leaching as Related to the NWWSI Repository Site". UCRL-15825, Preprint SANL-510-001, May 1986.

DATE REVIEWED: 1/6/86; Revised 6/23/87; 7/13/87

TYPE OF DATA

Leach and pH data.

MATERIALS/COMPONENTS

SRL 165 glass containing U, Cs, and Sr, (SRL U glass); SRL U glass containing added $^{237}Np$, $^{239}Pu$, and $^{241}Am$, (SRL A glass), J-13 water pre-equilibrated at 90°C for two weeks with Topopah Spring tuff, (EJ-13), tuff, 304L SS, air.

TEST CONDITIONS

Detailed test conditions have been presented by Bates (see related reports below) but are repeated here except for changes. Tests were run in type 304L stainless steel reaction vessels which contained the sample submerged in EJ-13 water with an air space at the top. Vessels were sealed from the environment with silicone gaskets and exposed to a gamma radiation field produced by a $^{60}Co$ source at $1x10^{4}$ rd/h. The temperature was maintained at 90°C. The test matrices were as follows: (1) two SRL U disks in pre-equilibrated J-13 water (EJ-13), Surface area/Volume (SA/V) = 0.3 $cm^{-1}$, R= gas volume/liquid volume =0.3; (2), two SRL A disks in EJ-13 water with a polished tuff core wafer, SA/V= 0.3 $cm^{-1}$, R= 0.3; (3) EJ-13, R= 0.3; (4) EJ-13 with a polished tuff core wafer, R= 0.3. Each matrix was run at 90°C for periods of 14, 28, 56, 91, and 182 days. Duplicate samples were run for each time period. When possible, the protocol of the Materials Characterization Center (MCC-1) was followed.

## METHODS OF DATA COLLECTION/ANALYSIS

Solutions were cooled to room temperature and analyzed for pH, cations by inductively coupled plasma spectroscopy (ICP), anions by ion chromatography (IC), uranium by atomic fluoresence (AF), Cs by atomic absorption spectroscopy (AA), and radionuclides by gamma and alpha counting, and dissolved gases by Van Slyke gas chromatography. The solid test components were measured for weight change and were analyzed by scanning electron microscopy (SEM) and associated energy dispersive X-ray analysis (SEM/EDS), secondary ion mass spectroscopy (SIMS), nuclear resonance profiling and ion microprobe.

## AMOUNT OF DATA

Tables;

1. Concentration of Fixed Nitrogen Species for blank, SRL U, and SRL A glass. Concentrations of $NO_2^-$,$NO_3^-$ and total in nanomoles/ml for EJ-13 and EJ-13 + tuff after 14, 28, 56, 91 and 182 days.

2. Concentration, Normalized Transuranic Release, and pH Values for Tests Containing SRL A Glass for EJ-13 and EJ-13 + tuff. Lists period in days, pH, concentrations for unfiltered, and acid strip reported in disintegrations/second per 100 lamda of solution and normalized release rate for Am, Pu and Np respectively.

Figures;

1. Variation of pH with time for the non-tuff containing tests; pH (6.5 to 8.0) vs time in days (0 to 200) for SRL A, SRL U, and EJ-13 tests.

2. Normalized loss for (a) Li, (b) Na, (c) B, and (d) mass for SRL A, SRL U, SRl A + tuff and SRL U + tuff. Normalized release rate in $g/m^2$ (0 to 6) vs time in $days^{1/2}$ (0 to 16).

3. SIMS profile of SRL U glass + tuff leached for 91 days showing lithium (7), boron (11), sodium (23) and iron (56). Intensity ratio to m/e (mass/ionic charge) of 28 (0 to 4) vs sputter time in minutes (0 to 84). (Indicates concentration of element vs depth in glass).

## UNCERTAINTIES IN DATA

Not dealt with.

## DEFICIENCIES/LIMITATIONS IN DATABASE

All tests showed gradually increasing acidity for 91 days with an actual reversal of the trend at 182 days. This observation was believed to result from loss of acid volatiles from the system because of slight leakage from the test vessels. Loss of $CO_2$ and $N_2$ from the gas phase would reduce the amount of bicarbonate in the solution phase and decrease the production of nitric acid by radiolysis.

## RELATED HLW REPORTS

Bates, John K., Fischer, Donald F., and Gerding, Thomas J., "The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part 1, SRL 165 Glass", ANL-85-62, (1985).

## KEY WORDS

experimental data, supporting data, weight change, ICP, IC, AF, AA, SEM, SEM/EDS, SIMS, laboratory, air, J-13 water, tuff, cobalt 60, high temperature, acidic solution, basic solution, doped glass, $^{237}Am$, $^{239}Pu$, $^{241}Am$

## COMMENTS

This report presents data on the influence of gamma irradiation on the reaction of actinide doped borosilicate glass (SRL 165 A and SRL 165 U) in a test environment containing tuff. This is a continuation of experiments at various radiation doses (in this case, 1 x $10^4$ Rad). The objective is to determine the effects of gamma radiation on air and groundwater and how these interact to change the pH of the leachate and the resulting interaction with and nuclear glass in tuff. In the gamma radiation field, nitric acid is generated by radiolysis of air; thus the solution becomes more acidic. This effect is counteracted by dissolution of the glass and buffered by the bicarbonate in the tuff. Major changes in groundwater in the blank tests show a rapid lowering of the pH to the buffered region (6.4). This pH would be maintained unless the buffering capacity of the groundwater was exceeded by acid production, or acid production was decreased because of depletion of $N_2$ from the gas phase. The radiation levels at the end of the containment period are expected to be less than 100 rd/hr or about a factor of 100 less than those in the experiments reported in this paper.

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

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

Related to issue 2.3.2.1.2 in the ISTP for the NWWSI Project which involves the rates of dissolution associated with the potential mechanisms of waste form dissolution.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory

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

Acton, C. F. and R. D. McCright, "Feasibility Assessment of Copper-Base Waste Package Container Materials in a Tuff Repository," UCID-20847, September 30, 1986

## DATE REVIEWED: 3/13/87

## TYPE OF DATA

Feasibility assessment

## MATERIALS/COMPONENTS

Copper (CDA 102), Al Group (CDA 613), Cu-Ni alloy (CDA 715)

## TEST CONDITIONS

Tuff environment, J-13 groundwater, $\gamma$-radiation

## METHODS OF DATA COLLECTION/ANALYSIS

N/A

## AMOUNT OF DATA

No original data; all tables and figures are taken from other publications. Sources are given.

## UNCERTAINTIES IN DATA

N/A

## DEFICIENCIES/LIMITATIONS IN DATABASE

N/A

KEYWORDS

feasibility assessment, laboratory, Yucca Mountain, J-13 water, tuff, gamma radiation field, copper base, CDA 102, CDA 613, CDA 715, corrosion (crevice), corrosion (pitting)

COMMENTS

The paper discusses the feasibility of using copper-base containers for HLW at the Nevada site. The conclusions are quite favorable. The authors agree that the extant data on questions such as the effect of $\gamma$-radiation on corrosion rates and the occurrence of localized corrosion are insufficient for final conclusions. Nevertheless, on the basis of the work so far completed (mainly HEDL-7612 for corrosion studies) the outlook is quite good.

No attempt is made to rank the three materials considered, nor is a number suggested for a recommended thickness for the container. The reliability of the data used, particularly of the geochemical data characterizing the environment, is not discussed. Since the conclusions concerning corrosion resistance depend heavily on this, the uncertainty might be greater than the authors claim it is. The issue of stress corrosion cracking also has not been seriously addressed.

RELATED HLW REPORTS

Many. In particular: W. N. Yunker, "Corrosion of Copper-Base Materials in Gamma Radiation," HEDL-7612, 1985.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to issue 2.2.4.1, rates of corrosion as a function of time for the various corrosion modes of the waste package container, in the ISTP for the Nevada Nuclear Waste Storage Investiation (NNWSI) Project.

(b) New Licensing Issues

(c) General Comments

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

(b) Author(s), Reference, Reference Availability: Van Konynenburg, R. A., "Radiation Chemical Effects in Experiments to Study the Reaction of Glass in an Environment of Gamma-Irradiated Air, Groundwater, and Tuff", UCRL-53719, May 1986.

DATE REVIEWED: 4/10/87; Revised 6/15/87

TYPE OF DATA

Discussion of kinetic modeling of chemical reactions induced by gamma radiation of air, groundwater and other waste package components.

MATERIALS/COMPONENTS

Considers experimental data reported by Bates et al. and Abrajano et al. (See related HLW reports below). This report considers experiments involving SRL U glass, SRL A glass; J-13 water pre-equilibrated at 90°C for two weeks with Topopah Spring tuff (EJ-13 water), tuff, 304L SS, and air.

TEST CONDITIONS

As reported by Bates and Abrajano, leach tests were run in stainless steel reaction vessels. The samples were submerged in about 16 ml of EJ-13 water with at least 4 ml of air at the top. These vessels were sealed from the environment and exposed to a gamma radiation field produced by a $^{60}Co$ source of $2x10^5$ (Bates) or $1x10^5$ rd/h (Abrajano) at a temperature of 90°C. Samples consisted of two glass disks or two glass disks with tuff. Tests for each of the glasses were run in duplicate for 7, 14, 28, and 56 days (Bates) or 14, 28, 56, 91, and 182 days (Abrajano). Similar tests were run on two blanks containing EJ-13 water and EJ-13 water plus tuff.

METHODS OF DATA COLLECTION/ANALYSIS

Details of data collection and analysis are reported in detail in the review of Bates et al. and Abrajano et. al. cited below.

AMOUNT OF DATA

Tables:
1. Composition of AISI standard type 304L stainless steel.
2. Composition of SRL glasses.
3. Composition of Topopah Spring tuff expressed as oxides.
4. Composition of "Equilibrated J-13" water at 20°C (first set of experiments).
5. Parameters influencing composition of gas and liquid phases. Parameter,(e.g., vapor pressure of water), value at 20°C, value at 90°C, reference.
6. Changes in compositions of gas and liquid phases due to heating, in vessels originally containing 16 ml of water. Gas phase volume, pressure, liquid phase volume, concentration of species at 20 and 90°C.
7. Composition of standard dry air.
8. Primary products of gamma irradiation of liquid water for pH of 5 to 9.
9. Reactions and rate constants for pure water at 25°C (from 4 sources).

Figures:
1. Nitrogen fixation in 2 x $10^5$ rd/h experiment, Increase in concentration of fixed nitrogen in $10^{-4}$ M (-.40 to 1.60) vs Time in days (0 to 60).
2. Nitrite-nitrate ratios in $10^4$ rd/h experiments, Ratio $[NO_2^-]$ (M)/$[NO_3^-]$(M), (0 to 7) vs Time in days (0 to 200).
3. Nitrite-Nitrate ratios in $2x10^5$ rd/h experiments, Ratio $[NO_2^-]$(M)/$[NO_3^-]$(M) (0 to 2) vs Time in days (0 to 60).

UNCERTAINTIES IN DATA

Uncertainties in anion analyses of ± 5%, dose ± 10%, yield (No. of particles of a particular species created or destroyed per 100 ev) ± 15%.

DEFICIENCIES/LIMITATIONS IN DATABASE

The author states, "Since a thoroughgoing computer model of the system of interest was not available, I elected to perform an approximate analysis of the radiation chemistry considering only the dominant reactions."

KEY WORDS

air, cobalt 60, data analysis, effect of radiation on leaching, gamma radiation field, J-13, kinetic model, SRL U glass, SRL A glass, theory, tuff

COMMENTS

This report discusses the formation of a number of species which could be formed by interaction of gamma radiation with components present in a repository setting. Initially, in this report an attempt to model the experimental results obtained in leach experiments by Bates et al and Abrajano et al is reported. Van Konynenburg used an equation developed by Burns et al., which predicts that the formation of fixed nitrogen (i.e., nitrites or nitrates), will be proportional to the ratio of the volume of air to liquid and the total dose. This equation gives a reasonable fit to the experimental data. Depending on the conditions, many possible reaction products can result from radiolysis. For the experiments considered here, the principal reactions include the following: (1) a net radiolysis of water into $H_2$ and $O_2$, (2) nitrogen fixation to $NO_2^-$ and $NO_3^-$ with the formation of an equivalent amount of $H^+$ which tends to lower the pH against the buffering action of dissolved carbonate, tuff, and glass, and (3) the formation of a colloidal $Fe^{+3}$ substances suspended in the solution as a result of interactions with the vessel walls. It should be noted that when groundwater first breeches the waste canister some 300 to 1000 years after closure, the gamma radiation dose rate will be at least 3 orders of magnitude below those used here.

RELATED HLW REPORTS

Bates, John K., Fischer, Donald F., and Gerding, Thomas J., "The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part 1, SRL 165 Glass", ANL-85-62, (1985).

Abrajano, T., Bates, J., Ebert, W., and Gerding, T., "The Effect of Gamma Radiation on Groundwater Chemistry and Glass Leaching as Related to the NWWSI Repository Site". UCRL-15825, Preprint SANL-510-001.

Burns, W. G., Hughes, A. E., Marples, J. A. C., Nelson, R. S., and Stoneham, A. M., "Effects of Radiation on the Leach Rates of Vitrified Radioactive Waste," J. Nucl. Mater. 107, 245 (1982).

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

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

Related to issue 2.4.3 in the ISTP for the Nevada Nuclear Waste Storage Investigation (NNWSI) Project concerning how the radionuclide species (i.e., paticles, colloids and solubles) change with time in the waste package.

(b) New Licensing Issues

(c) General Comments

## WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data:

Westinghouse Hanford Laboratory, P. O. Box 1970, Richland, Washington for the Nevada Nuclear Waste Storage Investigations Project (NNWSI)

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

H. D. Smith, "Zircaloy Spent Fuel Cladding Electrochemical Experiment at 170°C and 120 psia $H_2O$," HEDL-7545, April, 1986

DATE REVIEWED: January 19, 1987

TYPE OF DATA

There is no data. This is a research plan.

MATERIALS/COMPONENTS

Zircaloy spent fuel cladding from the H. B. Robinson fuel assembly B-05 (removed from service, May 6, 1974 after 799 full power days, av. burnup of 28.0 MWd/kgM and peak burnup, 31.4 MWd/kgM), identified as MCC Approved Testing Material ATM-101; cladding with surface oxide and cladding with the oxide removed to expose the bare metal.

TEST CONDITIONS

Two environments, considered to be critical, are used. The first occurs after 90 to 100 years with an unbreached container but with breached fuel containing water. This test is designed to expose cladding in 120 psi, 170°C deionized water in an autoclave. The second environment occurs after 1000 years and the canister is breached. Cladding is exposed to 90°C tuff-equilibrated J-13 water. Six experiments are planned. The first two tests are scoping tests and results will be used to refine future tests. Bundles of spent fuel cladding mimicing the configuration in repository storage will be placed in Hastelloy-276 autoclave for periods of 2, 6 and 12 months. The fuel with Zircaloy-4 plugged ends will be bundled in a hexagonal array, wrapped in 304 stainless steel sheet, clamped with stainless steel, and will sit on alumina plates. Alumina spacers will be used to electrically isolate the cladding from the autoclave. Some C-clamp specimens will be loaded to test for stress corrosion cracking.

## METHODS OF DATA COLLECTION/ANALYSIS

A thermocouple will be used to monitor the autoclave temperature, the pressure will be monitored, and the amount of water at the beginning and end of the test and any added water will be measured. The water level will be about one-half the distance to the top of the autoclave. Records will be kept in a dedicated HEDL notebook. At intervals in the test, 5 ml of water will be drawn to analyze for pH, Zr, $^{14}C$, and $^{137}Cs$. Evaluation after testing will use photography to document exposed specimens. Selected specimens will be prepared metallographically and observed with light microscopy and with the scanning electron microscopy. Auger analysis in conjunction with ion milling will be used to analyze thin film growth.

## AMOUNT OF DATA

This report gives no data from experimental tests. There are five figures. Four of these figures are "Section Diagrams" and "Sample Identifiers Correlated to the Cs-137 Gamma Scan of H.B. Robinson Fuel Rod Segments (J12C, N4C, C5T, and C5B)"; these show activity counts per 300 sec. vs. distance from the bottom in cm. The fifth figure is a "Schematic Cross Section of the Autoclave with the Spent Fuel Cladding Bundle in Place." There is one table which gives the "Distribution of Spent Fuel Specimens (from Figures 1, 2, 3, and 4) Between the Three Experimental Bundles."

## UNCERTAINTIES IN DATA

Corrosion rates at 180°C on the order of tens of angstroms may be detectable by profiling thin films with Auger analysis/ion milling techniques. Photographic and microscopic evaluation rely on comparative observations to identify and measure corrosion.

## DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

## KEYWORDS

Planned work, corrosion, surface film, pitting, visual examination radioactivity level simulated field, Yucca Mountain, J-13 water, deionized water, high temperature high pressure, cladding, spent fuel, Zircaloy, Zircaloy-4, $^{14}C$, $^{137}Cs$.

## COMMENTS

This seems to be a good experiment for scoping corrosion behavior under the conditions given. The sampling, apparatus, testing procedures, and specimen analyses appear to be planned well. The data from these tests will show whether corrosion does or does not occur within the testing time. There are no electrical measurements, and electrochemical measurements are the type of data needed to describe corrosion reactions and to predict long-term behavior. Tests with electrochemical connections should be considered for future planned tests. In the meantime, the data, as obtained from the tests as planned, should be useful.

## RELATED HLW REPORTS

Five reports are cited in the references; HEDL-7455, HEDL-TC-2562, PNL-5109, UCID-20172 (reviewed at NBS) and HEDL-7455 Rev. 1.

## APPLICABILITY OF DATA TO LICENSING

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.6 Potential damage and failure mechanism for spent fuel cladding

(b) New Licensing Issues

(c) General Comments

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data:

Westinghouse Hanford Company, P. O. Box 1970, Richland, Washington

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

"C-Ring Stress Corrosion Cracking Scoping Experiment for Zircaloy Spent Fuel Cladding", H. D. Smith, March 1986, HEDL-7546, Prepared for the US DOE, Office of Civilian Radioactive Waste Management, Contract No. DE-AC06-76FF02170

DATE REVIEWED: 4/2/87; Revised 6/24/87

TYPE OF DATA

There is no data because this is a research plan.

MATERIALS/COMPONENTS

Zircaloy cladding from Turkey Point spent fuel, some specimens will have a thick oxide coating (10 μm) and other specimens will have a thin oxide coating (3 μm).

TEST CONDITIONS

This "C-Ring" test method is patterned after ASTM G 38, "Standard Recommended Practice for Making and Using C-Ring Stress-Corrosion Test Specimens". The environment for this scoping test is 90°C tuff equilibrated J-13 well water. (Another experimental series, to be reported latter, will use an environment of 170°C water at 120 psi in an autoclave). The stress is applied by C-ring loading. The yield stress of the C-rings will be determined in air to establish load levels for the stress corrosion cracking (SCC) tests.

METHODS OF DATA COLLECTION/ANALYSIS

Each experiment will be monitored using a linear variable displacement transducer (LVDT). A time vs. deflection record will be kept and from these data, a failure load stress level can be defined. The experiment will be terminated at a predetermined deflection which is characteristic of failure. Specimens will be examined in the scanning electron microscope to study the fracture surface, the outside surface near the scc crack, and the relationship between the surface oxide layer fracture and the fracture of the metal. Failure rate vs. load under given environmental conditions will be determined. The chemistry of the water will be monitored regularly and adjusted if needed. Quality assurance procedures will be followed.

AMOUNT OF DATA

There is no data. There are three figures describing the experiment: Figure 1. "C-Ring" Experiment Apparatus. Arms with weights in place lowered to "C-Ring" stressing position; Figure 2. Schematic Cross Section of the Water Tank of the "C-Ring" Stress Corrosion Cracking Scoping Experiment Apparatus with the Anvils in Position Stressing a "C-Ring" Specimen; and Figure 3. Cladding "C-Ring" Specimen. Figure 1A in the appendix shows plots of the variation of the "apparent mechanical advantage" (R) versus the distance from the design load line (x).

UNCERTAINTIES IN DATA

Not addressed.

DEFICIENCIES/LIMITATIONS IN DATABASE

KEYWORDS

planned work, laboratory, Yucca Mountain, stress corrosion cracking (scc), corrosion, test, J-13 water, water, tuff, ambient temperature, high temperature, static (no flow), Zircaloy, mixed stress loading, spent fuel

COMMENTS

This test is described for use in a scoping experiment, and it is a practical test for this purpose. The circumferential stress in the "C-Ring" specimen is not uniform. The stress will vary through the specimen thickness, around the circumference to the middle of the arc and across the width of the ring. The transverse stress also varies and is a maximum at mid-width of the specimen and zero at the edges. The applied stress in the "C-Ring" test can be measured accurately with deflection methods. Surface oxide thickness can influence scc susceptibility. Solution pH can influence scc by causing the surface oxide to be unstable. An attempt should be made, during the microscopic analyses, to determine whether the failure is due to scc or some other form of local corrosion, such as hydrogen embrittlement, corrosion fatigue, etc. The absence of scc susceptibility after running this test would not be conclusive. Other tests such as slow-strain-rate tests, low frequency corrosion-fatigue tests, and electrochemically controlled scc tests should be conducted to characterize the material in terms of resistance to scc.

RELATED HLW REPORTS

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.6 Potential damage and failure mechanisms for spent fuel cladding

(b) New Licensing Issues

(c) General Comments

# WASTE PACKAGE DATA REVIEW

DATA SOURCE:

(a) Organization Producing Data:

Argonne National Laboratory, Argonne, Illinois 60439

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

Bates, John K., and Gerding, Thomas J., "One-Year Results of the NWWSI Unsaturated Test Procedure: SRL 165 Glass Application", ANL-85-41, August 1986.

DATE REVIEWED: 1/5/87; Revised 6/12/87

TYPE OF DATA

Leach data (unsaturated conditions).

MATERIALS/COMPONENTS

J-13 well water equilibrated with tuff at 90°C (referred to as EJ-13 water)· type 304 L stainless steel, tuff, glass made by mixing SRL-165 black frit with appropriate amount of $UO_2$, SrO, and $CsNO_3$ to provide a glass with approximatly 1% U, and 0.1% Sr and Cs.

TEST CONDITIONS

The unsaturated test procedure refers to the moisture content of the tuff and the fact that the glass test material is not totally immersed in groundwater. The reaction vessel allows J-13 water droplets of 0.1 ml per drop to drip at a predetermined leak rate onto the waste form, which in this case is a cylindrical doped SRL-165 glass. Water drips into a reservoir at the base of the test vessel to allow for simulation of unsaturated conditions at a temperature of 90°C and pressure of 1 atm. The glass specimen, representing the waste form, is held in position by a stainless steel holder consisting of perforated plates above and below the specimen, the plates were held together by stainless steel rods. The rods were welded to the bottom plate using Tungsten Inert Gas (TIG) welding. Groundwater may be circulated, by evaporation and condensation due to temperature gradients in the test apparatus, but this is not made clear in the report. See general comments below.

## METHODS OF DATA COLLECTION/ANALYSIS

Specimens representing two of the anticipated waste-package components (waste form and canister) are contacted intermittently by dripping water. The glass was analyzed for phase separation using x-ray diffraction (XRD) and scanning electron microscopy (SEM). The glass composition was determined by colorimetry (Si, P), atomic absorption (Cs), isotopic dilution mass spectrometry (B), and inductively coupled plasma spectroscopy (ICP), (all other elements). Many of the deposits, glass surfaces and steel parts of the test apparatus were characterized visually, by Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) and Secondary Ion Mass Spectrometry (SIMS).

## AMOUNT OF DATA

Figures:

1. NWWSI Waste Form Test Apparatus. (a) Cutaway view, (b) Schematic, (c) Selected parts.
2. Photograph of a Reacted Sample of Glass from Test F-4. Figures 3a-18 contain twenty one photomicrographs of selected reaction sites or reaction products at specified locations;
   analysis of top and bottom of canister by SIMS; and SIMS Spectrum of the Nonsensitized Surface of the Reference Type 304L Stainless Steel.

Appendix 3. Modified Test Vessel Design.

Tables:

1. Test Matrix for Unsaturated Tests.
2. Composition of SRL Glass Used in Testing.
3. General Observations of Canister Sections
4. General Observations of the Glass after Disassembly.
5. Water Loss During Testing.
6. Analyses of Equilibrated J-13 Water Used in Unsaturated Testing.
7. Results of the Blanks for the Unsaturated Tests.
8. Solution Results for the Continuous Tests.
9. Solution Analyses for the NWWSI Unsaturated Tests.
10. Results from the Dissolution of Tuff Cups.
11. Analyses Performed on Components from the Unsaturated Tests.
12. Component Weight Changes in NNWSI Unsaturated Tests.
13. Composition of 304 L Stainless Steel Used in the Unsaturated Tests.
14. SIMS Analysis of Tuff Samples.
15. Total B, Li, and U Release from the Waste Form.
16. Solution Results of Glass Parametric Test No. 1.
17. Test Conditions and Selected Results from the Analog Tests.

Appendix 1. Conditions and Selected Results of the Unsaturated Test Matrix.
Appendix 2. Detailed Solution Analyses for the Unsaturated Tests.

UNCERTAINTIES IN DATA

Uncertainties in some of the chemical analyses are discussed briefly.

DEFICIENCIES/LIMITATIONS IN DATABASE

The objective of tests was to obtain leach data as a function of time with a "reasonable" trend in elemental release required for modeling repository behavior was not achieved because apparently different release trends were observed owing to sensitization of stainless steel.

RELATED HLW REPORTS

J. K. Bates and T. J. Gerding, "NNWSI Phase II Materials Interaction Test Procedure and Preliminary Results," ANL-84-81 1984.

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

KEY WORDS

data analysis, experimental data, supporting data, x-ray diffraction, visual examination, weight change, SIMS, SEM/EDS, SEM, laboratory, air, J-13 water, tuff, high temperature, stainless steel, 304L stainless steel,doped SRL-165 glass, $^{238}U$,

COMMENTS

This report describes leach data obtained using an unsaturated test procedure. In this leach procedure, the waste form is not totally immersed in water but the method devised does allow liquid water to be in contact with the waste form if water is present and the temperature gradients in the canister are appropriate. The section of the report describing the means of water injection into the test apparatus is totally inadequate. In ANL 84-81 (1984), which is a more detailed report of the test method, the authors describe an injection system in which water and air are injected into the apparatus in prescribed amounts and intervals. In this report, the method described in ANL 84-81 is not mentioned. The statement that the "temperature differential between the waste package and the test vessel is based on the thermal equilibration of test component." could be interpreted as meaning that the water flow is driven by a temperature gradient. There is also some question concerning the pressure at which the measurements are made. Although it is stated that the pressure is 1 atm, van Konynenburg's analysis of similar measurements indicated higher pressures due to expansion of the initial air and the partial pressure of water at 90°C.

Much of this report deals with interactions, between the waste form, water, and stainless steel, resulting from sensitization of stainless steel due to tungsten-inert-gas weldments on the waste support holder. Since there may be weldments on the stainless steel canisters, the effect of sensitized stainless steel on the leaching kinetics of the waste form may be important. Most nuclear waste glasses may undergo leaching simultaneously by both hydration and matrix breakdown. Hydration initially occurs more rapidly than matrix breakdown but since it follows parabolic ($t^{1/2}$) kinetics, the penetration of the hydration front slows with time. When sensitized stainless steel is present, the formation of Fe, Ni, and Cr silicates increases the rate of matrix breakdown so that it may become the dominant leach process. Matrix breakdown is a process in which the constituents that form the matrix of the glass are simultaneously released so that normalized release rates of all the elements are the same. The kinetics are linear with time. The extent of interaction of leachate with stainless steel in the data obtained in this report varied broadly from extensive to slight.

<u>APPLICABILITY OF DATA TO LICENSING</u>:
[Ranking: key data ( ), supporting data (X)

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

This report is related to issue 2.3 concerning when, how, and at what rate radionuclides will be released from the waste form.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

DATA SOURCE:

(a) Organization Producing Data:

Hanford Engineering Development Laboratory, P. O. Box 1970, Richland, WA 99352

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

Einziger, R. E., "Test Plan for Long Term, Low-Temperature Oxidation of Spent Fuel, Series 1", HEDL-7560, June 1986.

DATE REVIEWED: 3/26/87

## TYPE OF DATA

Plan for low-temperature oxidation of spent fuel. Oxidation rate to be determined from weight gain as a function of time at specified temperatures.

## MATERIALS/COMPONENTS

Selected spent fuel from Turkey Point, air, water vapor, Ni/Cr crucibles.

## TEST CONDITIONS

Spent fuel samples consisting of fragments sized from -10/+24 mesh and -24/+60 mesh will be oxidized in dry air, (dew point below -55 OC), and moist air, (dew point of 80°C), at temperatures of 175, 130 and 110°C. Samples of 10 grams will be contained in Ni/Cr crucibles and heated in an aluminum block dry bath. Test duration will be 2 years. Time intervals between periodic weighings of 100 to 400 hours will be adjusted as data become available in order to obtain optimal weight gains. Mesh sizes 10, 24, and 60 correspond to 1.7, 0.71, and 0.25 mm respectively. Dew points of -55 and 80°C correspond to water vapor partial pressures of less than 0.016 and 355 torr respectively.

## METHODS OF DATA COLLECTION/ANALYSIS

Rate constants will be determined from weight gain data fit to models. Models assume grain boundary diffusion in early stages of oxidation followed by bulk diffusion. Post test samples will be examined by scanning electron microscopy (SEM) and x-ray diffraction (XRD) to obtain additional phase information.

AMOUNT OF DATA:

Tables:

1. Test Matrix.
2. Determination of $D_g$ (grain boundary diffusion constant) from Thermogravimetric Analysis (TGA) data.
3. Time Ranges when Bulk Diffusion Becomes Controlling Oxidation Mechanism.
4. Turkey Point Fuel Available for Testing.
4. Thermal Conductivity of Uranium Oxides.

Figures:

1. Rate Constant for Spent Fuel Oxidation Determined by TGA Testing, Rate constant ($10^{-9}$ to $10^{-3}$ $cm^2/h$) vs $10^4/T$ (19 to 26°$K^{-1}$).
2. Weight Gain Projections for 10g Sample Based on Single Mechanism Oxidation. Weight gain (0 to 150 mg) vs time (0 to 20,000 h)
3. Weight Gain Projections after Slow Grain Boundary Penetration. Weight gain (0 to 200 mg) vs time (0 to 20,000 h).
4. Oxidation of Spent Turkey Point PWR Fuel in Air at 200°C. [1-(3 delta O/M)$^{1/3}$] (0 to 0.20) vs $t^{1/2}$ (0 to 15 h $^{1/2}$).
5. Grain Boundary Diffusion of $O_2$ into Spent Fuel as a Function of Temperature Based on TGA data. Diffusion constant ($10^{-10}$ to $10^{-7}$ $cm^2/s$) vs $10^4/T$ $K^{-1}$ (20 to 26).
6. Time to Complete the Grain Boundary Diffusion Stage as a Function of Fragment Radius at 175, 130, and 110°C. Radius of fragment (0 to 2 mm) vs $t^{1/2}$ (0 to 140 $hrs^{1/2}$).
7. Cutting Diagram for Rods Used in Testing.
8. Relationship of Characterization and Test Rods in Assembly B17.
9. Gamma Scans of Companion Rods from Assembly B17. Relative activity (0 to 100) vs distance from bottom fuel pellet (0 to 150 inches).
10. SEM Examination of Fuel Fragments from Rod F6.
11. Dry Bath Oxidation System.
12. Dry bath with Blocks, Thermocouples and Gas Lines.
13. Positioning of Crucible and Fuel Sample in the Aluminum Thermal Blocks.
14. Placement of Thermocouples in Dry Bath Diagnostic Testing.
15. Sample Crucible.

UNCERTAINTIES IN DATA

Not applicable.

DEFICIENCIES/LIMITATIONS IN DATABASE

If diffusion along the grain boundaries is slow with respect to the test duration, measurements of weight gain utilizing fuel fragments will not reflect the rate limiting bulk diffusion step but will represent a combination of grain boundary and bulk diffusion.

KEY WORDS

planned work, oxidation of spent fuel, supporting data, diffusion model, weight change, SEM, XRD, laboratory, air, water vapor, spent fuel (PWR reactor), high temperature, ambient pressure,

COMMENTS

Spent fuel is a potential waste form for isolation in a nuclear waste repository. Oxidation of spent fuel is expected to have an effect on both the rate of leaching and the concentration of specific radionuclides in the leachate. This report deals with oxidation of spent fuel in breached Zircaloy cladding. Defected cladding may allow the spent fuel to oxidize to a more leachable higher oxidation state before the fuel comes into contact with groundwater. A plan is described for obtaining oxidation data in dry or moist air at temperatures in the range of 110 to 175°C. From previous measurements, the authors believe that oxidation of spent fuel by air involves an initial oxidation mechanism of grain boundary diffusion followed by a bulk diffusion process into the individual grains. This is a plausible concept but the data presented in support of it is not very convincing because only a single data point falls on the line purported to represent grain boundary diffusion. It is possible that the deviant point thought to represent grain boundary diffusion is due to random error in the measurements. Although the oxidation of spent fuel will not take place within leaktight Zircaloy cladding, the lifetime of cladding under repository conditions is uncertain. The conditions for the oxidation study in dry or moist air are very different. The moist air water pressure would be 355 torr as compared to 0.016 torr for the dry-air measurements. This could lead to different rates of oxidation because at a total pressure of one atmosphere the partial pressure of $O_2$ would be lowered. Also interaction of radiation from the spent fuel with water vapor might lead to formation of different gaseous species which could change the oxidation mechanism. Knowledge of rate constants for both grain boundary and bulk diffusion could provide an estimate of the overall oxidation rate of the spent fuel if it was possible to determine the time period during which each diffusion process was important.

RELATED HLW REPORTS

Einziger, R. E., and Woodley, R. E., "Low Temperature Spent Fuel Oxidation under Tuff Repository Conditions", HEDL-SA-

3271FP (1985). Proceedings of the Symposium on Waste Management, Tucson, Arizona, March 24-28 (1985).

Einziger, R. E., and Woodley, R. E., "Test Plan for Series 2 Thermogravimetric Analysis of Spent Fuel Oxidation," HEDL-7556, February (1986).

Einziger, R. E., and Woodley, R. E., "Evaluation of the Potential for Spent Fuel Oxidation under Tuff Repository Conditions," HEDL-7452, March (1985).

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

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

Related to issue 2.3.6.3 in the ISTP of the NWWSI Project. This issue concerns how the presence of defects alter the radionuclide retention capability of the waste form. Oxidation of the spent fuel through pinholes or other fissures is a potential failure mechanism.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA 94550

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

V.M. Oversby, "Spent Fuel as a Waste Form--Data Needs to Allow Long Term Performance Assessment Under Repository Disposal Conditions", UCRL-94659, December 1986.

DATE REVIEWED: 5/4/87; Revised 7/27/87

## TYPE OF DATA

(1) Scope of the Report

The report is an analysis and technical review of factors affecting radionuclide release from spent fuel under repository conditions. (See reports listed under Related HLW Reports for the original information and greater detail of the methods and results than are given in this report.) The paper presents an analysis [details of calculations not given in this report] of NRC and EPA regulations and from that analysis a ranking of the radionuclides in spent fuel is derived. Areas are suggested where more work is needed to support performance assessment calculations.

(2) Failure Mode or Phenomenon Studied

Dissolution of spent fuel and assembly components in high-level waste repositories.

## MATERIALS/COMPONENTS

Radionuclides for which release rates are discussed include: $^{241}Am$, $^{242}Am$, $^{242}Am$, $^{243}Am$, $^{14}C$, $^{242}Cm$, $^{245}Cm$, $^{246}Cm$, $^{135}Cs$, $^{129}I$, $^{94}Nb$, $^{59}Ni$, $^{63}Ni$, $^{237}Np$, $^{239}Np$, $^{107}Pd$, $^{238}Pu$, $^{239}Pu$, $^{240}Pu$, $^{241}Pu$, $^{242}Pu$, $^{226}Ra$, $^{79}Se$, $^{151}Sm$, $^{126}Sn$, $^{99}Tc$, $^{230}Th$, $^{233}U$, $^{234}U$, $^{235}U$, $^{236}U$, $^{238}U$, $^{93}Zr$.

Besides the spend fuel itself, other radioactive elements found in components are mentioned, specifically the nickel in stainless steels, the zirconium in Zircaloy, and the carbon-14 activation product in the Zircaloy.

## TEST CONDITIONS

(1) State of the Material being Tested

In the tests for which results are reviewed (see Reports HEDL-TME 85-22 and UCID-20926, Figures 1, 2, 3), the spent fuel used was PWR fuel of average burnup from the H.B. Robinson reactor. Bare fuel as well as fuel with the cladding hulls were included in the tests. Some Turkey Point bare fuel was also tested.

(2) Specimen Preparation

No information is given.

(3) Environment of the Material being Tested

The Nevada Nuclear Waste Storage Investigations (NNWSI) Series 2 dissolution test conditions were used (details describing these tests are not given in the report). The solution used for all cycles of the testing was J-13 well water, a dilute sodium bicarbonate groundwater.

METHODS OF DATA COLLECTION/ANALYSIS

The author discusses and compares the NRC rule (10 CFR 60) and Environmental Protection Agency standards ( 40 CFR 191) for HLW disposal in geologic repositories. The EPA standards set limits on the cumulative release of radionuclides to the accessible environment for 10,000 years. Release limits are set for individual radionuclides and for total activity released. For individual radionuclides, there must be a probability of less than 0.1 for releases to exceed one part in 100,000 of the inventory at 1000 years after repository closure and a probability of less than 0.001 for the releases to exceed 10 times those values. The NRC has rules to implement the EPA standards. Siting Guidelines (10 CFR 960) also require long range performance assessment of proposed repositories and a comparison of performance prior to specific site selection. The comparison is based on two calculations of system performance for 100,000 years. The first calculation uses a specified high value for release of radionuclides from the engineered barrier system, and the second uses a realistic site-specific value. These calculations [not given in the report] require performance predictions for ten times longer than the NRC rule. The NRC rule requires that the release rate of any radionuclide from the engineered barrier system following the 300-1000 year containment period be less than one part in 100,000 of the inventory of that radionuclide present after 1000 years after closure. The most stringent control that must be demonstrated is one part in $10^5$ of a radionuclide inventory at 1000 years after closure or one part in $10^8$ of the total inventory present 1000 years after emplacement, whichever is greater. For most radionuclides the total inventory value is applicable.

The analysis of release rates indicate that americium and plutonium require the most reduction in release, that is, the greatest release rate control of the radionuclides. Suggested methods to accomplish this are lower waste form dissolution rates, demonstration of reduction in transportable species resulting from precipitation reactions, retardation of transport due to ion exchange or other sorption processes, or long groundwater travel times.

The results of NNWSI Series 2 dissolution tests of the effect of leaching solutions on the concentrations of radionuclides in stored fuel are quoted. Tests were run in cycles of approximately six months in the same solution. At the end of each cycle the solution and fuel samples were removed from the quartz tests vessel and transferred to a new vessel with fresh solution. Solution samples were taken periodically during a cycle. At the end of a cycle, the vessel was rinsed and acid stripped to recover any precipitated solution.

<u>AMOUNT OF DATA</u>

There are four tables, five figures, and seventeen references cited.

Table I - "Release rate control required by 10 CFR 60," lists ten radionuclides whose release must be controlled to 1 part in 100,000 of their own inventory at 1000 years after repository closure and, twenty-three radionuclides for which the calculated release rate applies and the factors [for which the calculations are not given in this report] by which their release rates may exceed 1 part in 100,000 of their own inventory at 1000 years after repository closure.

Table II - "Release rate control based on chemical element," lists the control of release rate for 18 chemical elements based on the most stringent control required for any isotope of that element, in parts in 100,000 of the 1000 year post-closure inventory of that element.

Table III - "Comparison of NRC and EPA allowed releases assuming that no nuclide contributes more than 0.035 EPA units to the sum of release ratios. Comparison is made at the edge of the engineered barrier system," lists the ratios of NRC/EPA allowed releases for 17 elements.

Table IV - "Summary of release data for NNWSI Series 2 H.B. Robinson bare fuel samples, Cycles 1 and 2, conducted at ambient hot cell temperature," lists Total Release in parts in $10^5$, and Percent in Solution for nine elements.

Figure 1 - "Concentration of uranium in solution for the four cycles of the NNWSI Series 2 dissolution tests. Test run at ambient hot cell temperature in quartz vessel using bare fuel with split cladding hulls present in the test." Data are plotted for 0 to 5 ppm uranium for tests of up to 240 days duration for four different cycles of tests.

Figure 2 - "Activity in solution for cesium-137, NNWSI Series 2 tests, cycles 2, 3, and 4. Release for cycle 1 was about 40 times higher than for cycle 2." Data for tests of up to 240 days duration ranging from 0 to 3 microcuries/ml are plotted.

Figure 3 - "Activity of technetium in solution, NNWSI Series 2 tests." Data for four different cycles for tests of up to 240 days duration are plotted for pCi/ml values ranging from 0 to 500.

Figure 4 - "Correlation of fission gas release and rapid release fraction of cesium from CANDU fuel." Measured and calculated values for stable xenon release ranging from 0.01 to 10.0 percent are plotted versus $^{137}Cs$ release values ranging from 0.01 to 10.0 percent.

Figure 5 - "Uranium concentrations in unfiltered solutions for NNWSI Series 3 tests and for the H.B. Robinson Series 2 bare fuel sample. See text for symbol explanation." Concentration in micrograms per milliliter for seven solutions is plotted against test durations up to 240 days.

<u>UNCERTAINTIES IN DATA</u>

The review discusses several factors for which available data are inadequate to characterize radionuclide release from waste-form components. These factors are described in three categories:
(1) Effects of sample preparation,
(2) Sample storage conditions,
(3) Experiment design variables.
See the next section for details of the deficiencies in the database.

<u>DEFICIENCIES/LIMITATIONS IN DATABASE</u>

The author identifies six areas where new data are most needed to judge repository license application:

(1) the effect of reactor type and burnup on dissolution properties of spent fuel; fuel dissolution probably will not depend heavily on these parameters, but population variability must be addressed in licensing arguments.

(2) dissolution studies on stainless steel clad fuel; part of the existing inventory of spent fuel, and fuel in use, is clad in stainless steel and no dissolution data exist.

(3) dissolution studies of oxidized spent fuel; the effect of oxidation state on dissolution rate and solubility is needed to assess the effects in the repository environment and the effects of air storage of test specimens.

(4) dissolution studies using assembly components; there are no data for the rate of radionuclide release from such components in aqueous solutions.

(5) inventory and release characteristics of carbon-14; data are needed on both release in air and release into aqueous solutions of carbon-14.

(6) thermodynamic properties of solids that might limit radionuclide solubility; silicate minerals may limit the solubility of uranium and affect the dissolution properties of spent fuel. Data for uranium silicates are sparse to nonexistent as well as data for compounds thought to limit solubility of actinides. Modelling of long term behavior of geochemical systems depends on good thermodynamic data for the relevant phases.

KEY WORDS

data analysis; literature review; leaching solution analysis; simulated field; air; J-13 water; ambient temperature; stainless steel; zirconium base; spent fuel (PWR reactor); spent fuel (BWR reactor); $^{241}Am$, $^{242}Am$, $^{242}Am$, $^{243}Am$, $^{14}C$, $^{242}Cm$, $^{245}Cm$, $^{246}Cm$, $^{135}Cs$, $^{129}I$, $^{94}Nb$, $^{59}Ni$, $^{63}Ni$, $^{237}Np$, $^{239}Np$, $^{107}Pd$, $^{238}Pu$, $^{239}Pu$, $^{240}Pu$, $^{241}Pu$, $^{242}Pu$, $^{226}Ra$, $^{79}Se$, $^{151}Sm$, $^{126}Sn$, $^{99}Tc$, $^{230}Th$, $^{233}U$, $^{234}U$, $^{235}U$, $^{236}U$, $^{238}U$, $^{93}Zr$.

COMMENTS

A comprehensive review of spent fuel radionuclide release factors and data are presented with identification of needs for further study. No new data are included. See the section "Deficiencies/Limitations in Database" for the data needed to provide an adequate database for characterizing radionuclide release from waste-form components.

RELATED HLW REPORTS
UCRL-94222
HEDL-TME 85-22
UCID-20926
UCRL-90855
UCRL-94708
PNL-5109
UCRL-94633
HEDL-TME 84-30
See also 40 CFR Part 191, Federal Register vol. 50, No. 182 (1985);
10 CFR Part 60, U.S. Government Printing Office (1983);
10 CFR Part 960, Federal Register vol. 49, No. 236 (1984).

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.3 When, how, and at what rate will radionuclides be released from the waste form?

(b) New Licensing Issues

(c) General Comments

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# WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory

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

L. B. Ballou and R. D. McCright, "LLNL, Attachment 1 to letter dated 8 March 1985" to M. Steindler, Argonne National Laboratory, as background information for Materials Review Board ad hoc panel review of NNWSI (and other) repository project corrosion testing programs

DATE REVIEWED: 10-1-85; Revised 12-3-85; 7-20-87

TYPE OF DATA

(1) List of planned tests: Dry oxidation, corrosion, stress corrosion cracking, localized corrosion test data

MATERIALS/COMPONENTS

Various rocks and glasses. For corrosion tests: Zircaloy, 304L, 316L, 321, Incoloy 825 stainless steels, cast iron, various steels and alloys.

TEST CONDITIONS

Mostly tuff environment, J-13 water alone and with additions (e.g., chlorides).

METHODS OF DATA COLLECTION/ANALYSIS

N/A

AMOUNT OF DATA

N/A

UNCERTAINTIES IN DATA

N/A

DEFICIENCIES/LIMITATIONS IN DATABASE

N/A

KEY WORDS

Corrosion tests; SCC tests

COMMENTS

This report is a list of experiments planned or in progress. Neither results nor detailed description of experimental conditions are given. It also covers experiments outside corrosion.

APPLICABILITY OF DATA TO LICENSING
[Ranking: Key data ( ), supporting data (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

Related to issue 2.2.4, potential corrosion failure modes for the waste package container, in the ISTP for the Nevada Nuclear Waste Storage Investigation (NNWSI) Project.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Lawrence Livermore National Laboratory

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

L. B. Ballou and R. D. McCright," LLNL, Attachment 2 to letter dated 8 March 1985" to M. Steindler, Argonne National Laboratory, as background information for Materials Review Board ad hoc panel review of NNWSI (and other) repository project corrosion testing programs, MRB-0418.

DATE REVIEWED: 10-1-85; Revised 12-3-85; 7-21-87

TYPE OF DATA

Plans for future testing: Corrosion, pitting, stress corrosion cracking. This is a proposed plan for testing Cu and Cu alloys as a possible package material in tuff environment and possibly basalt. A small amount of initial testing should occur in FY 85.

MATERIALS/COMPONENTS

Copper and Cu alloys, CDA 102, CDA 172, CDA 181, CDA 613, CDA 715; also as entire canister

TEST CONDITIONS

Tuff geochemical environment, with and without "$\gamma$-radiation

METHODS OF DATA COLLECTION/ANALYSIS

Principally electrochemical methods

AMOUNT OF DATA

None

UNCERTAINTIES IN DATA

N/A

DEFICIENCIES/LIMITATIONS IN DATABASE

N/A

KEY WORDS

Copper, copper alloys, corrosion, tuff

COMMENTS

Cu and Cu alloys will be examined as possible container materials, not only from the corrosion standpoint, but also from the mechanical and economic.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to issue 2.2.4, potential corrosion failure modes for the waste package container, in the ISTP for the Nevada Nuclear Waste Storage Investigation (NNWSI) Project.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

Rockwell International, Richland, Washington

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

R. P. Anantatmula, "Effects of Grande Ronde Basalt Groundwater Composition and Temperature on the Corrosion of Low-Carbon Steel in the Presence of Basalt-Bentonite Packing," (RHO-BW-SA-391 P), August 1985

DATE REVIEWED: 1/28/87; Revised 4/30/87

TYPE OF DATA

Experimental data. Weight loss corrosion tests. Statistical analysis.

MATERIALS/COMPONENTS

1020 AISI Steel packed in 75% basalt, 25% bentonite, in the presence of solutions containing various amounts of NaCl, NaF, $Na_2SO_4$ and $Na_2CO_3$

MATERIALS/COMPONENTS

Steel as received (hot-rolled). T = 100°C and 250°C in pressure vessels. No oxygen.

METHODS OF DATA COLLECTION/ANALYSIS

Weight loss after 4 weeks. Analysis by the Plackett-Burman statistical method.

AMOUNT OF DATA

1 Table. Weight losses for various solution compositions and temperatures.

UNCERTAINTIES IN DATA

95% confidence level.

DEFICIENCIES/LIMITATIONS IN DATABASE

Not addressed.

KEYWORDS

experimental data, Plackett-Burman statistical design, weight change, laboratory, deionized, Cl, $F^-$, $SO_4^{--}$, $CO_3^{--}$, basalt, bentonite, high temperature, carbon steel, 1020 carbon steel, hot-rolled, chloride, basalt, bentonite

COMMENTS

It is an extremely limited test, so that its relevance is minor. Can be taken as indicating that groundwater composition is not too important under reducing conditions.

The conclusion "if resaturation of the repository occurs at a higher temperature (200 to 250°C) the effect on corrosion of low-carbon steel in the presence of the anions within the concentration range tested will be negligible" is not justified by the data. [page 6, paragraph 2]. Lack of statistical significance does not imply absence of a real effect.

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

(a) Relationship to Waste Package Performance Issues Already Identified

This document address BWIP ISTP issues 2.2.4, what are the corrosion modes of the waste package container and 2.2.4.3, how does the packing material affect the corrosion rates?

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data:

Pacific Northwest Laboratory, Richland, Washington 99352

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

S. G. Pitman, "Slow-Strain-Rate Testing of 9%Cr, 1%Mo Wrought Steel and ASTM A27 Cast Steel in Hanford Grande Ronde Groundwater", SD-BWI-TS-008, August 1984.

DATE REVIEWED: 2/26/87; Revised 7/31/87

## TYPE OF DATA

1. Scope: Experimental Results

2. Failure Mode: Environmental Induced Cracking; Stress Corrosion Cracking

## MATERIALS/COMPONENTS

2 Candidate Container Alloys

9Cr-1-Mo Steel (ASTM A387 Gr. 9)
(normalized at 900°C for 52 min, air cooled, tempered at 720°C)

ASTM A27 Cast Steel
(tested as cast)

The specific compositions of the alloys are given in tables 1 and 2.
The specimens were procured and fabricated according to MD-82-1, Rev. 0.
The third candidate alloy was the subject of another report (see ref).

## TEST CONDITIONS

Slow Strain Rate Tests

Standard Proc: MD-82-7, "Slow-Strain-Rate Studies, Unirradiated"
Strain Rates: $1x10^{-4}$, $1x10^{-6}$ and $2x10^{-7}$/s
Autoclave environment (150°C)
Simulated Grande Ronde Groundwater

Flowing (9 ml/h), Through crushed basalt then autoclave
Deaerated with either pure Ar or Ar-20% $O_2$
Dissolved $O_2$ levels: Ar = <1ppm and Ar-20% $O_2$ = 8ppm $O_2$

METHODS OF DATA COLLECTION/ANALYSIS

Load and Displacement measurements
- Yield Strength
- Ultimate Tensile Strength

Direct Measurement of Sample
- Reduction in area
- Strain to Failure

AMOUNT OF DATA

6 Tables:

1. Composition of 9Cr-1Mo Steel
2. Compostion of ASTM A27 Steel
3. Composition of Umtanum Flow Basalt
4. Composition of Hanford Grande Ronde (basalt) Groundwater
5. Results of SSR Tests on 9Cr-1Mo Steel at 150°C
6. Results of SSR Tests on ASTM A27 Steel at 150°C

5 Figures:

1. Reduction in Area (0 to 70%) vs. Displacement Rate ($10^{-7}$ to $10^{-3}$) for
   9Cr-1Mo Steel at 150°C in air and groundwater.
2. Load (0 to 4500 lbs.) vs. Displacement (0 to 0.5 in) for 9Cr-1Mo steel at 150°C in groundwater.
3. Fractography of 9Cr-1Mo steel tested at $1 \times 10^{-6}$ in/s in groundwater.
4. Reduction in Area (0 to 70%) vs. Displacement Rate (1e-7 to 1e-3) for A27 Steel 150°C in air and groundwater.
5. SEM Fractography of A27 Steel tested at 150°C in groundwater showing ductile "MVC" fracture.

UNCERTAINTIES IN DATA

"The basalt rock and groundwater employed in these tests were the BWIP reference compositions at time of usage. Current (FY-1985) reference compositions are GR-4 groundwater and Cohassett flow basalt. Differences in composition between Cohassett and Umtanum basalt are slight and no difference in corrosion behavior are expected to result."

DEFICIENCIES/LIMITATIONS IN DATABASE

"It is recognized that the groundwater flow rate, oxygen concentration levels, specimen environment and imposed stresses may not be identical to those anticipated for the waste container in a repository. However, for the stated purpose of assessing relative susceptibility of different canister materials to environmental assisted cracking, the test conditions are thought to be sufficient."

KEYWORDS

experimental data, supporting data, microscopy (SEM), tensile testing, visual examination, slow strain rate, laboratory testing, basalt groundwater, high temperature, steel (A27 and A387), cast steel, elongation, tensile strength, yield strength, corrosion (SCC), hydrogen embrittlement

COMMENTS

1. The author assumes that hydrogen embrittlement and SCC are separate and distinctly different phenomena.

2. The author assumes that, since a two week pre-exposure had no effect on the SSR test ductility at $1 \times 10^{-4}$/s, the failure mechanism is SCC. (Presumably, what the authors means is that the mechanism of SCC was some mechanism other than hydrogen embrittlement.) However, no reduced ductility was found for tests conducted in the environment at this strain rate. If this strain rate was too fast to cause a reduction in the ductility in the environment, then why should it be slow enough to test the hydrogen embrittlement hypothesis. If hydrogen embrittlement is responsible for the observed crack propagation, then hydrogen diffusion could be the rate limiting process and it would not change its rate with the testing environment. There is insufficient evidence to conclude that hydrogen embrittlement is not responsible for the observed crack propagation.

3. The author concludes that SCC is not occurring based on the presence of dimples on the fracture surface (even though numerous secondary cracks and a reduced ductility were observed). Mechanisms have been proposed for hydrogen embrittlement and SCC which would be consistent with a dimple morphology. As a result, it is premature to conclude that there is not environmental contribution to crack propagation especially when a reduction in the ductility and secondary cracks are observed.

RELATED HLW REPORTS

S. G. Pitman, Environmental Testing of AISI 1020 Steel in Hanford Grande Ronde Groundwater, SD-BWI-TI-152, Pacific Northwest Lab., Richland, WA.

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

(a) Relationship to Waste Package Performance Issues Already Identified

This paper addresses BWIP ISTP issues 2.2.4.1, the corrosion rates for various corrosion modes of the waste package container, and 2.2.4.2, the effect of radiation on the corrosion behavior of the waste container.

(b) New Licensing Issues

(c) General Comments

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data

Rockwell Hanford Operation

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

Shu-Chien Yung, Robert T. Toyooka and Tristram B. McCall, "Thermal Analysis of Waste Package Preliminary Reliability Assessment," RHO-BW-SA-509P, presented at: Symposium on Radioactive Waste Management '86, Tucson, Arizona, March 2-6, 1986.

## DATE REVIEWED: 2/5/87; Revised 6/30/87

## TYPE OF DATA

A three-dimensional integrated model was used to simulate and predict thermal conditions for the BWIP waste package and its environment. Axial temperature gradients in the waste form and container are predicted. The predicted temperature histories of the waste package container are employed to assess the container lifetimes. Calculations are made from a theoretical model describing the time dependence of the temperature at various places in the repository.

## MATERIALS/COMPONENTS

Consolidated spent fuel (CSF), Intact spent fuel assembly (SFA), West Valley High-Level Waste (WVHLW)

## TEST CONDITIONS

The assumption of the model are:

(1) The repository and its environment are in a homogeneous basalt flow and extend vertically to the boundaries of the problems investigated.

(2) All waste packages are simultaneously emplaced in the basalt repository.

(3) All components of the waste package are made of isotropic and homogeneous materials.

(4) Materials properties remain constant in each computer run.

(5) The heat of vaporization and condensation of groundwater in the host rock and convective transport of heat are not considered.

METHODS OF DATA COLLECTION/ANALYSIS

Calculation of temperatures as a function of time and position via the three-dimensional integrated model, Heating 5.

AMOUNT OF DATA

One Table and 10 Figures:

TABLE:

1. Important Temperatures from HEATING 5 computation results - Design-allowable temperatures and peak calculated temperatures for consolidated spent fuel, spent fuel assembly and West Valley High Level Waste.

FIGURES:

1. Diagram Illustrating Waste Package Terminology.

2. Underground Repository Layout.

3. Integrated Three Dimensional Thermal Model Based on Assumption of Geometric Symmetry and Waste Package Simultaneous Emplacement.

4. Detailed XZ Plane Dimensions of the Integrated Three-Dimensional Model.

5. Temperature Histories in and Near Consolidated Spent Fuel Waste Package in the Nominal Case, Calculated by the Integrated Thermal Model, for 1-10000 years, in some points: waste (axial center), container (end), borehole (inner surface), basalt (1.6m from waste center), emplacement room center, temperature range: 50-300°C.

6. Axial Temperature Profiles in Consolidated Spent Fuel Waste Form Midplane, 1, 5, 10, 25, 50 years after emplacement. For distance along the waste form of 0-4m in the temperature range of 100-300°C.

7. Axial Temperature Profiles in Container for Consolidated Spent Fuel Waste Form, 1, 5, 10, 25, 50 years after emplacement. For distances along the waste form of 0-4m and temperature range of 100-300°C.

8. Temperature Profiles in the Near Field of the Consolidated Spent Fuel Waste Package, 1, 5, 10, 25, 50 years after emplacement. For distances from waste package center of 0-2m and temperature range of 50-250°C.

9. Isoterms in the XZ Plane through Consolidated Spent Fuel Waste Package Center, 1, 5, 25, 50 years after Emplacement. For distances from waste package center of 0-3m and temperature range of 100-200°C.

10. Far Field Temperature Profiles in YZ Plane through Center of Consolidated Spent Fuel Waste Package, 50, 100, 500, and 1000 years after emplacement. For depths of 0-2000m below ground surface and temperature range of 0-250°C.

UNCERTAINTIES IN DATA

The decay power and the thermal conductivity of the waste form and packing have been varied in their estimated ranges. It was determined that the conductivities of the waste form and the packing are the most influential parameters affecting the temperature profiles. The ranges considered in the study showed that a temperature difference of more than 70°C may result from the uncertainty of the conductivities.

DEFICIENCIES/LIMITATIONS IN DATABASE

Neither the heat of vaporization and condensation of ground water in the host rock nor the convective transport of heat were considered in the model utilized here.

KEY WORDS

model/metodology; waste form; physical properties; data analysis; three dimensional integrated model; thermal analysis simulation; air; basalt; commercial high level waste (CHLW); spent fuel; thermal profiles; thermal instability

COMMENTS

This report is only a theoretical evaluation without any experimental results to validate the results. The modeling approach that was taken is significant in that it simultaneously provides both the thermal fields of the waste package and its near-field and far-field environment.

The fact that the heat of vaporization and condensation of the groundwater in the host rock was not considered could be very important in case of significant groundwater flow through the repository site.

RELATED HLW REPORTS

BMI/ONWI-517
BMI/ONWI-612

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

(a) Relationship to Waste Package Performance Issues Already Identified

This document addresses basalt ISTP issue No. 2.3.7 (how does the waste form design accomodate all potential waste package conditions) by calculating the thermal history of the waste package and repository area due to the waste form. Three different waste forms were studied.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data:

Corrosion Technology Section, Westinghouse Hanford Co., P. O. Box 1978, Richland, Washington 99352.

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

F. Brehm, J. M. Lutton, C. L. Rivera, H. P. Maffei, A. P. Bohringer, D. D. Paine and L. A. Pingel, "BWIP General Corrosion Studies, Summary Report of Activities in FY-1984", B047154, 1984.

DATE REVIEWED: 2/5/87; Revised 6/18/87

## TYPE OF DATA

Experimental

## MATERIALS/COMPONENTS

Test coupons of cast and wrought AISI 1020 steel, Fe-9Cr-1Mo steel, Cupro-nickel 90-10, weldments of these materials, OFHC copper and phosphorus-deoxidized copper. AISI 1020 steel with artificial pits. Ferrallium 255, Hastelloy C-276, Inconel 600 and Inconel 625 were obtained as alternate materials with higher corrosion resistance, and these will be used for future testing.

## TEST CONDITIONS

An air-steam chamber (ovens with exposure boxes to operate at 150°C, 200°C, 250°C and 300°C) to simulate the environment of the preclosure period; post closure anoxic, high temperature environment (200°C, 1250 psig) simulated by static pressure vessels (Parr type) and autoclaves containing basalt-bentonite packing, Grande Ronde #4 synthetic ground water and corrosion specimens. Anion effects (specific amounts of Cl, F, SO4, or CO3 added to test solution at 100°C and 200°C) on 48 specimens of 9Cr-1MO-Fe, Packing material used in the tests was a 3:1 basalt:bentonite mixture.

## METHODS OF DATA COLLECTION/ANALYSIS

Weight loss determinations; electrode potential measurements, pit count, pit diameter and pit area measurements

## AMOUNT OF DATA

The eight figures are listed as follows.

Fig. 1. Operator installing a four vessel rack in oven. Two other racks can be seen, one on each level. Negative 8401740-13CN

Fig. 2. Air/Steam test with atmosphere chamber installed. The cover flange of the box has been removed to show the coupon racks in place. Negative 8401740-19CN

Fig. 3. Autoclave flow diagram

Fig. 4. Riffle sample splitter

Fig. 5. BWIP General corrosion test specimen summary

Fig. 6. Average corrosion rates (and standard deviations)

Fig. 7. BWIP Corrosion test-100°, anion effect on corrosion of 9Cr-1Mo-Fe

Fig. 8. BWIP Corrosion test-200°C, anion effect on corrosion of 9Cr-1Mo-Fe.

There are three numbered tables which are;

Table 1. Composition of actual and synthetic Grande Ronde 4 solutions,

Table 2. Reagents required for preparation of one liter basic stock solution, and

Table 3. Reagents for preparation of one liter of stock solution. There is one table with no number which lists "Compiled Data for Wrought AISI Steel Coupons"

UNCERTAINITIES IN DATA

Not addressed by authors.

DEFICIENCIES/LIMITATIONS IN DATABASE

Data collected and reported in the anionic effects tests do not give accurate analyses of corrosion rates due to limitations of the analytical balance which was used for weighing the specimens.

KEYWORDS

Planned work, experimental data, measurements, simulated groundwater, basalt, bentonite, high temperature, steel, cast and wrought 1020 and 1025 carbon steels, weld, corrosion, pitting, chloride, fluoride, sulfate, carbonate, preclosure, postclosure

COMMENTS

Equipment was wet up and tested for the conduct of three types of tests on candidate waste package materials and in some cases, their weldments. Candidate materials and alternative materials were obtained. These tests simulated repository environmental conditions before closure, after closure and a third test determined the effects of anionic species. Some pitting studies were conducted, but results were not conclusive. This type of simulated testing is valuable in producing data on the durability of materials under the environments of the repository before and after closure. These tests provide an indication of reactivity of these materials on a short term basis. Tests were conducted to check out the equipment and additional tests were reported to be in progress and results should be available by now. Additional electrochemical measurements should be carried out to supplement these data and to identify the corrosion processes.

RELATED HLW REPORTS

Westinghouse Hanford Company reports on corrosion studies in years preceding and following the period of this report.

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.2.4 regarding potential corrosion failure modes for the waste package container, 2.2.4.1 dealing with corrosion rates,
2.2.4.3 dealing with effects of packing materials on corrosion

(b) New Licensing Issues

(c) General Comments

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data

Pacific Northwest Laboratory

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

Pitman, S. G., "Enviromechnical testing of AISI 1020 steel in Hanford Grande Ronde Groundwater", B023959, July 1983

**DATE REVIEWED**: 5/19/87; Revised 7/7/87

## TYPE OF DATA

Experimental, environmentally assisted cracking

## MATERIALS/COMPONENTS

1020 steel waste canister

## TEST CONDITIONS

Hot-rolled wrught 1020 steel. Slow-strain-rate tests in air and Grande Ronde groundwater, 150°C, refreshed autoclave system

## METHODS OF DATA COLLECTION/ANALYSIS

Slow-strain-rate tensile test with LT and TL orientations
SEM observations

## AMOUNT OF DATA

Tables listing compositions of 1020-steel test material, Umtatum flow basalt and Hanford Grande Ronde basalt groundwater

Table giving detailed results of 20 slow-strain-rate tests in 150°C groundwater, 150°C air and 20°C air. Strain rates of $10^{-4}$ and $2 \times 10^{-7}$/s, with 1020-steel samples tested on longitudinal and transverse orientations.

Three figures plotting data from Table (above):
Figure 3 - Yield and ultimate strength (35 to 70 ksi) versus strain rate ($10^{-4}$ and $2 \times 10^{-7}$/s) for 1020 steel (LT orientation) in air and groundwater.

Figure 4 - Similar to Figure 3. Reduction in area (45 to 65%) and elongation (25 to 30%) plotted as function of strain rate.

Figure 5 - Similar to FIgure 4. Data for 1020 steel tested in TL orientation. 20 to 60% reduction in area and 15 to 25% elongation.

Optical micrograph of 1020 steel structure, 100x and 250x

Macrograph of slow-strain-rate specimen immediately after testing. Specimen strained to failure in 150°C groundwater at $2 \times 10^{-7}$/s; 21 day test.

Fifteen SEM photographs of fracture surfaces of slow strain rate test specimens. Includes illustration of pitting attack.

UNCERTAINTIES IN DATA

Author states that groundwater used in this study differs somewhat from composition now being considered as the reference Grande Ronde groundwater but is unlikely that differences affect environmentally assisted cracking kinetics. Specific groundwater composition differences not described in report.

DEFICIENCIES/LIMITATIONS IN DATABASE

Author states that definitive conclusions concerning structural barrier material selection and design are beyond scope of document.

KEYWORDS

experimental data, corrosion, simulated field, simulated groundwater, Cl, ambient temperature, high temperature, carbon steel, 1020 carbon steel, hot worked, slow strain rate, groundwater, elongation, tensile strength, yield strength, cracking (environmentally assisted)

COMMENTS

Author does not state thickness of hot rolled steel plate used to prepare test specimens. There are significant structural differences in hot rolled plate in the thicknesses required for canister construction as compared with thinner gauge plate. These structural differences may affect EAC test results.

Data provide clear indication of environmentally assisted cracking for 1020 steel tested at low strain rate ($2 \times 10^{-7}$/s) in Grande Ronde groundwater. Further studies are needed to relate conclusion to structural barrier material selection.

RELATED HLW REPORTS

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

(a) Relationship to Waste Package Performance Issues Already Identified

This paper addresses BWIP ISTP issue 2.2.4, what are the various corrosion modes for the waste package container?

(b) New Licensing Issues

(c) General Comments

WASTE PACKAGE DATA REVIEW

DATA SOURCE:

(a) Organization Producing Data

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

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

Barney, G. Scott, Lane, Douglas L., Allen, Carlton C., and Jones, Thomas C., "Sorption and Desorption Reactions of Radionuclides with a Crushed Basalt-Bentonite Packing Material", RHO-BW-SA-416 P, April 1986.

DATE REVIEWED: 1/10/87; Revised 4/12/87

TYPE OF DATA

Laboratory sorption and desorption measurements of selected radionuclides, ($^{239}Pu$, $^{240}Pu$, $^{237}Np$, $^{238}U$, $^{99}Tc$, $^{79}Se$, and $^{226}Ra$) on fresh or hydrothermally altered packing materials. Twelve run Plackett-Burman statistical design to determine important variables in groundwater composition.

MATERIALS/COMPONENTS

Umtanum basalt characterized as sample RUE-2 (-120 to 230 mesh), commercial Wyoming bentonite clay (-400 mesh), synthetic groundwater and hydrothermally altered packing material prepared using a basalt/bentonite weight ratio of 3/1, synthetic groundwater/solids ratio of 2 in rocking, or rolling autoclaves at 300°C, and 30MPa for 1 month. The synthetic groundwater was selected to simulate Grande Ronde Basalt groundwater that had been altered by interaction with the basalt-bentonite mixture. The model for this groundwater was a solution generated by reacting a crushed basalt-bentonite mixture (1:1 by weight) with synthetic Grande Ronde basalt groundwater at 150°C for three months. A synthetic composition based on the analysis of the resulting water was used as the groundwater.

TEST CONDITIONS

Equilibrated samples (at 90°C) of packing material, radioactive tracers, and groundwater were used for measuring the radioactive distribution between the solid and liquid phases. The radionuclide oxidation state was controlled either by removing sufficient oxygen by evacuation to allow the solids and dissolved redox couples to control oxidation states, or by making the solutions .01 M in hydrazine.

METHODS OF DATA COLLECTION/ANALYSIS

Distribution of radioactivity between the liquid and solid phases of the samples was determined from the initial and the final solution activity as established by counting techniques. The basalt and bentonite were characterized before and after hydrothermal alteration using X-ray diffraction, scanning electron microscopy and scanning transmission electron microscopy. Analysis of groundwater was made using inductively coupled plasma, atomic emission spectrometry for elements such as silicon, potassium and sodium, ion chromatography for $F^-$, $Cl^-$, and $SO_4^{2-}$, total carbon analyzer for carbonate, and ion selective electrode for sulfide. Sorption data are plotted using the Freundlich isotherm equation.

AMOUNT OF DATA:
Figures:

1. Concentration of Technetium (log Tc,-4 to -7 M) Remaining in Solution Versus Initial Hydrazine Concentration (log $N_2H_4$, -4 to -1 M) for Sorption Experiments with Packing Material.

The data in the following figures were obtained at 90°C using altered packing material.

2 and 3. Cation (2) and Anion (3) Concentrations (1-1,000 mg/L) Versus Time(0 to 24 d) for Groundwater Reactions.

4. Sorption Rate Curve for Uranium on Altered Packing Material (log U concentration, -9 to -4 M versus time, 0 to 30 d)

5. First-order Plots for Uranium Sorption. (log $C/C_0$, -3 to 0 versus time, 0 to 30 d).

6, 7, 8. Sorption Rate Curves for Neptunium, Selenium, and Radium respectively. (log Np, -8 to -3 M; log Se, -8 to -4 M; log Ra, -11 to -7 M) versus Time, 0 to 30 d)

9, 10, 11. Sorption Isotherms for Uranium, Neptunium, and Selenium respectively using (a) Basalt, or (b) 0.05 M Hydrazine as Redox Control: log S (Sorption, mol/g) vs log C (Concentration, M). Typical order of magnitude sorption and concentration ranges are (-10 to -6) and (-9 to -5) respectively.

12. Sorption Isotherms for Technetium using 0.05 M Hydrazine as Redox control, log S mol/g (-9 to -5) vs log C, M (-9 to -5).

13. Uranium Concentration Desorbed into the Groundwater for Consecutive Desorption Equilibrations, log C, M (-5 to -7) vs equilibration number (1 to 8).
14, 15. Desorption Isotherms for Uranium in absence and presence of 0.05 M Hydrazine respectively: log S, mol/g (-7 to -6) vs log C, M (-7 to -4).

16, 17. Desorption Isotherms of Neptunium in absence and presence of 0.05 M Hydrazine respectively: log S, mol/g (-7 to -5) vs log C, M (-8 to -5).

18, 19, 20. Desorption Isotherms for Selenium and Technetium in presence of .05 M hydrazine and Radium respectively, log S, mol/g, vs log C, M: Se, (-7 to -6) vs (-7 to -5): Tc, (-6.5 to -5.5) vs (-7 to -6): Ra, (-10.5 to -9.5) vs (-11 to -9).

The data in the following figures used un-altered packing material.

21, 22. Calculated Concentration in solution and effect of Hysteresis along a 10 cm Column Filled with Packing Material for
Uranium(IV) at (a) 600 d and (b) 100, 200 400 and 600 d and for Selenium(II) respectively at, (a) 50 d and (b) 50 and 100 d: U, (a) log $C/C_0$ (-4 to 0) vs Distance (1 to 10 cm), (b) log $C/C_0$ (-6 to -0) vs Distance (1 to 10 cm): Se, log $C/C_0$ (-5 to 0) vs Distance (1 to 10 cm).
23. Log Normal Probability Plot for Plutonium Sorption on Packing Materials, log $K_d$ (ml/g x $10^{-3}$) (1 to 1000) vs Probability of Value < $K_d$(%) (.01 to 99.99)

Tables:
1. Comparison of Synthetic "Steady State" Groundwater Composition with Solution from Hydrothermal Experiments.
2. Stock Solutions Used in Preparation of the Steady State Synthetic Groundwater.
3. Packing Material Alteration Run Parameters.
4. Solution Analysis of Packing Material Alteration Tests.
5. Oxidation States of Radionuclides Reduced by 0.01 M Hydrazine in Groundwater Solutions.
6. Groundwater Composition (mg/l) versus Time for Reaction with Altered Packing Material at 90°C.

7, 8, 9, 10, 11. Uranium, Neptunium, Selenium, Technetium, and Radium Sorption Kinetics Data respectively.

12. First Order Rate Constants for Uranium and Neptunium Sorption on Altered Packing Material at 90°C.
13. Radionuclide Distribution Between Groundwater and Altered Packing Material at 90°C (average of duplicate measurements).
14. Freundlich Constants for Sorption of Radionuclides on Altered Packing Material at 90°C.

15. Radionuclide Desorption data for U, Np, Se, Tc and Ra from Altered Packing Material into Groundwater at 90°C.
16. Freundlich Constants for Desorption of Radionuclides from Altered Packing Material into Groundwater at 90°C.
17. Ratios of Freundlich N values for Radionuclide Sorption and Desorption at 90°C.
18. Composition of Synthetic Groundwater used in the Plackett-Burman Experimental Design.

19, 20, 21, 22, 23. Data from the Plackett-Burman Experiments for Uranium, Neptunium, Plutonium, Selenium, and Technetium Sorption respectively, on Altered and Fresh Packing Material at 90°C.

24. Significant Groundwater Variables for Radionuclide Sorption on Packing Material at 90°C concluded from the Plackett-Burman experiments.
25. Effect of Carbonate Concentration on $K_d$ Values (distribution coefficients) of Uranium, Neptunium and Technetium.
26. Representative Formation Constants for 1:1 Actinide Complexes with Groundwater Ligands.
27. Difference in Radionuclide Sorption between Altered and Fresh Packing Materials.

UNCERTAINTIES IN DATA

Statistical analysis was performed on fit of data to Freundlich isotherm equation. Standard errors from scatter in data are reported.

DEFICIENCIES/LIMITATIONS IN DATABASE

Not dealt with.

KEY WORDS

Adsorption of Radionuclides, Ar, Basalt, Basic solution,Bentonite, Kinetics of Adsorption, Data analysis, Desorption, Experimental Data, Freundlich isotherm, high temperature, laboratory, $^{237}$Np, Placket-Burman Test, $^{239}$Pu, $^{226}$Ra, $^{79}$Se, simulated groundwater, $^{99}$Tc, $^{238}$U

COMMENTS

The radionuclides with the exception of $^{99}$Tc are strongly adsorbed on the basalt-bentonite packing material. The basalt provides a reducing environment in which most of the radionuclides will slowly be reduced to lower oxidation states in which form they are strongly adsorbed on the packing material. The adsorption of $^{99}$Tc by basalt requires that oxygen potentials lower than those obtained in this work in the absence of hydrazine, be obtained. Only the adsorption of $^{79}$Se was significantly different in the hydrothermally altered packing material. The sorption and desorption data presented in this report are empirical distribution coefficients and sorption and desorption isotherms. They are steady state values obtained over weeks or months of equilibration time but do not represent thermodynamic equilibrium. Sorption rates were generally much faster than desorption rates.

The addition of hydrazine as a means of obtaining reduced forms of the radionuclides could possiblly interfere with some radionuclide reactions. Kelmers et al have suggested a number of potential problems relative to the use of hydrazine in this type of experiment.

RELATED HLW REPORTS

Kelmers, A. D., Kessler, J. H., Arnold, W. D., Meyer, R. E., Cutshall, N. H., Jacobs, G. K., and Lee, S. Y., "Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects, Report for Oct-Dec 1983," NUREG/CF-3581, vol 1, ORNL/TM-9191/VI, Oak Ridge National Laboratory, Oak Ridge, Tenn.

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

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

This document addresses Basalt ISTP issue No. 2.14 (How does the packing material control the composition of the groundwater passing through it?). It deals with the sorption and desorption of the radionuclides leached from the waste form after a waste container breach. This will have an effect on the rate of escape of waste package radionuclides into the environment.

(b) New Licensing Issues

(c) General Comments

# WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

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

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

C.M. Jantzen, "Methods of Simulating Low Redox Potential (Eh) for a Basalt Repository," Materials Research Society Proceedings, 1978

DATE REVIEWED: 6/16/87

TYPE OF DATA

Experimental study.
Glass leaching and Eh-pH relationships in simulated basalt repository conditions.

MATERIALS/COMPONENTS

SRL 165 glass, ductile iron.

TEST CONDITIONS

Deionized water and GR-3 basaltic groundwater were used as leachants. Ductile iron bars and crushed Hanford Umtanum basalt were used as redox-active solids. Deoxygenated experiments were run in a glove box continually purged with argon.

METHODS OF DATA COLLECTION/ANALYSIS

Solution analyses were carried out using inductively coupled plasma (ICP), ion chromatography (IC), and atomic absorption (AA). Solution Eh and pH were monitored continuously in situ. The Eh measurements were made using a Pt electrode. Monolithic samples and filtered precipitates were dried at 90 degrees C for one hour. Surfaces and precipitates were examined by x-ray diffraction. Glass monolith surfaces were examined by electron microprobe.

AMOUNT OF DATA

Three figures:

1. Eh-pH changes measured (+/- 0.5 V) for deoxygenated deionized water and Umtanum basalt and the Eh-pH changes measured for deoxygenated GR-3 simulated basaltic groundwater. (Plot of Eh, 1 V to -1 V, vs pH, 0 to 14)
2. Eh-pH relations measured when SRL 165 waste glass and ductile iron are present in deionized water under oxic and anoxic conditions. Boundaries which are dependent on the amount of iron in solution are calculated for the actual iron concentrations found in the solutions. (Two plots of Eh, 1 V to -1 V, vs pH, 0 to 14)
3. Concentrations of Si, Fe, B, and Na leached from SRL 165 waste glass under oxic conditions with ductile iron present, under oxic conditions with no ductile iron present and under anoxic conditions with ductile iron present. All samples in deionized water at 70°C. (Leach periods 4 to 28 days)

UNCERTAINTIES IN DATA

Solution analyses showed poor reproducibility when colloids were present, even when the solutions were acidified.

DEFICIENCIES/LIMITATIONS IN DATABASE

Not addressed by authors.

KEYWORDS

Experimental data, deionized water, GR-3 water, basalt, leaching, DHLW

COMMENTS

In this paper, redox-active solids (crushed basalt and ductile iron) are used to control the oxidation potential of waste glass leachant solutions. Crushed basalt was found to be the most reactive material to maintain a negative (i.e., reducing, anoxic) Eh. Reproducing the basaltic repository redox environment using materials that will actually be present is certainly a better approach than adjusting Eh values by adding hydrazine or other foreign materials to the solution, as has been done in other studies.

The experimental data are used to show that the redox characteristics of the leachant electrolyte have a significant influence on leaching behavior. These redox characteristics, i.e., the ability to act as an oxidizing or reducing agent, are assumed to be represented by a measured potential, Eh. Further, some interpretation of the data is given to illustrate several specific phenomena which distinguish oxic (high Eh) from anoxic (low Eh) conditions. For example, the corrosion of iron and glass were shown to be synergistic, with each enhancing the corrosion of the other. However, the presence of oxygen to convert neutral iron to the ferrous ion was a key element in this behavior, so that mutually-induced corrosion should be less severe in anoxic environments such as those expected in basalt repositories.

Certainly, the relative oxidizing power of the leachant and the specific chemical species present are important in determining leaching behavior. While the present work contributes to establishing Eh as a tool for predicting leaching behavior, the effects of the host rock and metallic components of the environment could probably be described just as well by considering the leaching solution chemistry, without applying the Eh concept. However, Eh measurements are fast and easy to make (subject to the limitations discussed below), and have the advantage of summing up several variables in one numerical value. This introduces a potential pitfall: the same Eh value can be measured for different solutions. For example, when the redox characteristics of a solution are dominated by a single redox couple, e.g. $Fe^{+2}/Fe^{+3}$, Eh is determined by the ratio, not the actual concentrations, of the two species. Any combination of concentrations giving the same ratio also gives the same Eh. However, the concentrations determine the extent of possible chemical reactions. As a result, Eh gives an indication of the tendency of various reactions to occur (the driving force), but no indication of how long they will continue (the capacity). These questions have not been addressed in the present paper or in other related papers reviewed to date. For this reason, strict quantitative interpretation of the results with respect to determining extents of reaction from Eh values, which the authors avoid, must be viewed with caution.

The Eh measurement method used is a matter of potential concern. In the present work, Eh was measured using a Pt electrode. There is evidence that this method is not always satisfactory. Grenthe, for example, in KBS Technical Report no. 90, points out that either a low redox buffer capacity or poisons in the electrolyte can make the measured Eh values unrepresentative of the redox potential of the system. In addition, there is often a high degree of scatter in measurements made with a Pt electrode. A gold electrode has been recommended as a better choice. The authors of the present study discuss some of the limitations of the method, and it must be assumed that their measurements were conducted carefully. They reported that stable and reproducible Eh values were measured at Pt electrodes when iron was present in sufficient quantities in the ferrous and ferric states.

The potential drop across the Pt-leachant interface depends on the nature of both the solid and solution phases. The Pt electrode is highly inert in leachant solutions, i.e., it does not dissolve or react with the components normally present except perhaps to form a stable oxide on the surface. The glass-leachant interface, however, is a site of chemical reactions which depend on the chemistries of the glass and the leachant, and their interactions (hydration and dissolution of the glass, alkalization of the solution, etc) with each other. The Eh of the glass-leachant system, if it could be measured, would change as the system approached steady state. In the slow flow conditions expected in repositories, a steady state situation will be reached in which both phases are modified in the glass-leachant interfacial region where Eh is determined. The steady state redox characteristics at the interface will determine long term leaching behavior. The Pt probe senses changes in the redox characteristics of the solution in contact with the waste glass as this approach to steady state occurs, as shown in Figure 2 of the paper by the convergence of the data to the equilibrium calculated time. Distinctly different behavior is seen under oxic and anoxic conditions in this work. This result is important in two respects. It indicates that the anoxic conditions expected in the basalt repository should be less aggressive toward the glass waste, and that laboratory measurements of leaching should be carried out under anoxic conditions to be representative of repository behavior.

RELATED HLW REPORTS


1. C. M. Jantzen, "Effects of Eh (Oxidation Potential) on Borosilicate Waste Glass Durability," Second International Symposium on Ceramics in Nuclear Waste Management, 1984.

2. C. M. Jantzen and G. G. Wicks, "Control of Oxidation Potential for Basalt Repository Simulation Tests," Mat. Res. Soc. Proc. Vol. 44, page 29, 1985.

3. J. E. Mendel, Sci. Basis for Nuclear Waste Management VI, D. C. Brookins, ed., Elsevier Publ. Co., New York 1-7 (1983).

4. G. K. Jacobs and M. J. Apted, EOS Trans. Amer. Geophys. Union 62, 1065 (1981).

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

(a) Relationship to Waste Package Performance Issues Already Identified

This paper address BWIP ISTP issues 2.3, how will the radionuclides be released from the waste form 2.3.3, what colloids will be formed 2.3.5, how does the waste container material (and packing material) alter the radionuclide release rate.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data:

Swanson Engineering Associates Corporation, McMurray, PA

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

R. H. Mallett, "Buckling Design Criteria for Waste Package Disposal Containers in Mined Salt Repositories", BMI/ONWI-597, December 1986

DATE REVIEWED: 6/16/1987

TYPE OF DATA

1. Scope: This document is a survey of the literature on buckling analysis and experiments; no new theoretical development or buckling experiments were conducted. The purpose of this work was to provide guidance in establishing a waste-container design criteria to ensure protection against buckling of the container

2. Failure Mode: Elastic, elastic-plastic and plastic buckling

MATERIALS/COMPONENTS

Waste disposal container of low carbon steel

No experiments were performed; however, the survey focuses on low-carbon steels and the properties of these alloys.

TEST CONDITIONS

This document is a survey of the literature on buckling analysis and experiments; no new tests or experiments were performed for this document.

METHODS OF DATA COLLECTION/ANALYSIS

This document is a survey of the literature on buckling analysis and experiments. The results of buckling experiments are compared to the predictions of different analytical models. No new experiments or analyses are presented.

AMOUNT OF DATA

12 Tables:

3-1. Summary of Waste Package Design Features (Container and Canister length, diameter and thickness also borehole information)

3-2. Summary of Waste Package Performance Parameters (temperatures, heat loads, corrosion penetrations and corrosion allowances)

3-3. Comparison of Low Carbon Steel Specifications (Chemistry and physical properties of container material, AISI 1018 and ASTM 216 steels)

3-4. ASME Boiler and Pressure Vessel Code Design Stress Intensity Values (Nominal composition of steel, yield strength, ultimate tensile strength and critical stress intensity for metal at different temperatures)

4-1. Reference Disposal Container Length Parameters

4-2. Reference Disposal Container Thickness Parameters

4-3. Reference Disposal Container Thick-Wall Stress

4-4. Reference Disposal Container Ovality Effect

4-5. Reference Disposal Container Buckling

4-6. Minimum (R/t) for Elastic Buckling and Maximum (Et/E) for Elastic-Plastic Buckling

4-7. Recent Cylinder Buckling Results

4-8. Small Cylinder Buckling Results

22 Figures:

3-1. Conceptual Waste Disposal Container Design (diagram)

3-2. ASME Code Buckling Chart for Factor A (Length to Outside Diameter ratio) (Factor A)

3-3. ASME Code Buckling Chart for Factor B (10-5 to 100 Factor A)
(2,500 to 25,000 Factor B)

3-4. Creep Behavior for Salt (Time, 0-1.6x10-7 seconds) (axial strain, 0-10%)

3-5. Defense High-Level Waste Package Performance (0-150°C temperature, 15-20 MPa pressure and 0-1.0 cm.

UNCERTAINTIES IN DATA

The buckling analyses neglect the effects of transient pressure, seismic loading, shear loading and corrosion other than uniform. Also, interactions such as creep, radiation-induced creep, aging of the metal (thermal and radiation induced), radiation-induced corrosion and stress corrosion are neglected. The properties of the material are assumed uniform and inhomogeneities such as welds, weld heat affected zones, casting defects (inclusion and voids) are neglected.

DEFICIENCIES/LIMITATIONS IN DATABASE

The waste disposal container can be treated in a buckling analysis as a long cylinder. Neglect of the support provided by the end closure is conservative and will not significantly alter the results of the analysis. The waste disposal container must be analyzed as a thick wall cylinder. The use of average stresses in the basic buckling equations is an approximation which must be verified by testing. The collapse pressure of a thick walled cylinder is strongly dependent on the work hardening characteristics of the material. Imperfections in the container will increase the ovality of the container reducing the collapse pressure. However, for practical imperfections the reduction in the collapse pressure should not be significant. The cylinder collapse test results reviewed indicate that buckling of a thick wall cylinder does not result in loss of wall continuity. That is, buckling of a waste disposal container onto the waste form may not result in leaking. However, the tensile stresses resulting from buckling may lead to failure by other mechanisms. As a result, after the retrieval period, buckling of the container does not by itself constitute failure. The basic equations for buckling overestimate the critical buckling pressure for thin wall cylinders and overestimate the critical pressure for thick wall cylinders. As a result, these equations are conservative estimates of the critical pressure. The experimental results reviewed in this report indicated that finite-element analyses frequently result in predictions for the critical collapse pressure, which are no better than the predictions of the simple relationships. However, a finite element analysis can predict the critical pressure within 3 percent. The simple buckling equations underestimate the critical collapse pressure and the use of a load factor (defined as the ratio of the critical collapse pressure to the maximum expected service pressure) of 1.5 or 3, as is used in external pressure buckling design standards, should be a conservative design criteria. However, it is assumed that the geometry, material and applied loading are specified with conservatism appropriate to their uncertainty.

KEYWORDS

literature review, design, salt, steel, collapse load tests, waste form (CHLW, DHLW and spent fuel) modulus of elasticity, tangent modulus, yield strength, tensile strength, stress, strain, ovality, buckling, elastic buckling, plastic buckling, and elastic-plastic buckling

COMMENTS

This is not a critical review.

RELATED HLW REPORTS

American Society of Mechanical Engineers, 1983. ASME Boiler and Pressure Vessel Code, Nuclear Power Plant Components, ASME, New York. Bathe, K. J., 1976.

ADINA - A Finite Element Program for Automatic Dynamic Incremental Nonlinear Analysis, Report 82448-1, Acoustics and Vibration Laboratory, Mechanical Engineering Department, Massachusetts Institute of Technology, Cambridge MA. Crosthwaithe, J. L., J. N. Barrie and K. Nuttall, 1982. Design, Fabrication and Testing of a Prototype Stressed-Shell Fuel Isolation Container, Report AECL-6823, Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada DeSalvo, G. J., and H. Becker, 1957.

Handbook of Structural Stability, Part III - Buckling of Curved Plates and Shells, Report NACA-TN-3783, National Advisory Committee for Aeronautics, Washington DC. Hibbitt, Karlsson, 1981.

ABAQUS Computer Program Manuals, Volumes 1-4, Sorenson, Inc., Providence, RI. Huang, N. C. and P. D. Pattillo, 1982.

"Collapse of Oil Well Casing", J. Pressure Vessel Technology, 104m, pp. 36-41. Lockheed Missiles and Space Co., Inc. 1974.

BOSOR5, A Computer Program for Buckling of Elestic-Plastic Complex Shells of Revolution Including Large Deflection and Creep, Report LMSC-D407166, Lockheed Missiles and Space Company, Inc., Sunnyvale, CA. MARC Analysis Corporation and control Data Corporation, 1971.

MARC-CDC Nonlinear Finite Element Analysis Program, MARC Analysis Corporation and Control Data Corporation, Minneapolis, MN. Timoshenko, S. P. and Gere, J. M., 1961. Theory of Elastic Stability, Second Edition, McGraw Hill, New York.

APPLICABILITY OF DATA TO LICENSING
[Ranking: Key Data ( ), Supporting Data (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

The information in this report is pertains to ISTP issue 2.2.3 "What are the possible mechanical failure modes for the waste package container".

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

DATA SOURCE:

(a) Organization Producing Data:

Brookhaven National Laboratory, Upton, New York 11973

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

Levy, Paul W., "Radiation Damage Studies on Natural Rock Salt from Various Geological Localities of Interest to the Radioactive Waste Disposal Program," Nuclear Technology, 60 231-243, (1983).

DATE REVIEWED: 4/27/87

TYPE OF DATA

Radiation damage of rock salt by 1.5 MeV electron beam which is identical to damage produced by gamma radiation. Emphasis is on sodium colloid formation in the rock salt.

MATERIALS/COMPONENTS

Fourteen natural rock salt samples were irradiated by a 1.5 MeV electron beam.

TEST CONDITIONS

Samples are irradiated at constant temperature and extent of radiation damage is determined by optical measurements.

METHODS OF DATA COLLECTION/ANALYSIS

Extent of radiation damage is determined by optical absorption methods. Measurements are made as a function of temperature, dose, and strain in the crystals.

AMOUNT OF DATA:
Figures:
1. Appearance of rock salt as function of distance from spent fuel element in the Radioactive Waste Disposal Demonstration Project, Lyons Kansas.
2. Schematic of test radiation equipment.
3. Typical optical absorption and luminesence data.
4. Colloid concentration versus irradiation time curves as a function of temperature. Absorption Coefficient (0 to 50 $cm^{-1}$) vs Irradiation Temperature (100 to 300°C) vs Irradiation Time (0 to 10000 s).
5. Colloid formation in 14 natural rock salt samples irradiated at 150°C at a dose rate of $1.2x10^8$ rd/h.

Colloid Band Area (.1 to 50 arbitrary) vs Time (1 to $10^4$ s).
6. Colloid growth curves for natural rock salt from WIPP site recorded using strained crystals. Absorption at 2.14 eV, (0 to 50 $cm^{-1}$ vs irradiation time (0 to $9x10^3$ s) for 11%, 3.9% and undeformed crystals at 150°C, 120 Mrd/h)
7. Colloid formation in natural rock salt at an irradiation temperature of 150°C and dose rates of 30, 60 and 120 Mrd/h Absorption Coefficient (0 to 40 $cm^{-1}$) vs dose, (0 to 200 Mrad).
8. A black and white version of a colored photomicrograph of irradiated rock salt showing regions of F centers and colloidal sodium metal.

Tables:
1. Constants for 14 specimens for the equation, mole fraction NaCl converted to colloidal sodium = $Ct^n$ where C and n are constants and t is the time in seconds.
2. Impurities in colloid-rich and colloid-free areas in irradiated natural rock salt.
3. Percent sodium metal colloid expected in rock salt at canister interfaces for $10^{10}$ and $2x10^{10}$ rd, (about 50 to 400 y dose rate at $2x10^4$ rd/h).

UNCERTAINTIES IN DATA

Not dealt with.

DEFICIENCIES/LIMITATIONS IN DATABASE

The author states that because of the differences in dose rates, irradiation times, and rapidly applied stresses in laboratory experiments in contrast to anticipated dose rates, irradiation times and stresses under repository conditions, an accurate estimate of the total amount of radiation induced colloid and its spatial distribution requires appreciably more data than is presently available. To extrapolate from laboratory to repository conditions requires a better understanding of the radiation-damage formation kinetics in rock salt.

KEY WORDS

brine, chlorine, colloidal sodium in SRP, experimental data, gamma radiation field, high temperature, laboratory, radiation damage, radiation damage of rock salt

## COMMENTS

This report presents experimental work on radiation induced sodium metal colloid formation in rock salt. The technique involves bombardment of rock salt with a high energy (1.5 MeV) electron beam which is equivalent to the effect produced by gamma ray recoil electrons. This work is of importance to salt repositories because of the drastic change in pH which could take place in the repository environment if chlorine is lost from the rock salt and at some later time, large amounts of sodium colloid react with brine. The experimental data show that the induction period for colloid formation is shortened with strained samples, increases on a unit dose basis as the dose rate decreases, and appears to be affected by the salt impurity level, being suppressed in regions of crystals containing about 1% calcium and sulfur. The colloid formation rate is low or negligible below irradiation temperatures of 100 to 115, increases to a broad maximum at 150 to 175 then decreases to a negligible level at 275 to 300°C. Using the $C(\text{dose})^n$ relationship to estimate the colloid formed in actual repositories indicates that in 50 to 400 years, a dose of $10^{10}$ rad will convert .1 and 10%, and $2\times10^{10}$ rad will convert between 1 and 50% of the salt to colloidal sodium. In the laboratory cleaved or broken irradiated samples emit the odor of chlorine. Obviously, the fate of chlorine in the irradiated rock salt is very important. The authors plan to attempt to detect the escape of chlorine from irradiated samples using a mass spectrometer detector. Whether chlorine escapes from the rock salt or can limit the sodium colloid buildup by some type of recombination reaction is an important problem for the salt repository.

## RELATED HLW REPORTS

Levy, P. W. and Kierstad, J. A., "Very Rough Preliminary Estimate of the Colloidal Sodium Induced in Rock Salt by Radioactive Waste Canister Radiation"., Mat. Res. Soc. Symp. Proc., Elsevier Science Publ. Co., Vol 26 (1984) Pg 727-734.

## APPLICABILITY OF DATA TO LICENSING:

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

(a) Relationship to Waste Package Performance Issues Already Identified

(b) New Licensing Issues

(c) General Comments

None of the ISTP issues previously identified appear to specifically relate to the interaction of brine with colloidal sodium in rock salt. Such an interaction could lead to a large change in pH which would drastically change the local waste canister environment.

Draft Copy

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data:

Office of Nuclear Waste Isolation, Battelle Memorial Institute, 505 King Ave., Columbus, OH 43201-2693

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

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

## DATE REVIEWED: 6/19/87

## TYPE OF DATA

1. Scope: This document is a report of the August 1985 meeting of the engineering review group (ERG) where the salt repository project (SRP) salt irradiation effects program was reviewed; no new tests or experiments were performed for this document and no data is presented in this document. This review is the seventh in the series of regular ERG reviews conducted for ONWI. For this review, the ERG reviewed the work on irradiation effects at Pacific Northwest Laboratory and Brookhaven National Laboratory which was supported by the SRP and completed at the time of the review (see "Pertinent Documents").

2. Failure Mode: For a salt repository, the concern is that radiation induced changes in the chemical and physical properties of the near-field environment will impact waste package performance with respect to any of the potential failure modes.

## MATERIALS/COMPONENTS

The experiments reviewed by the ERG were conducted on single crystals of pure NaCl for the purpose of modeling the behavior of the bedded salt environment.

## TEST CONDITIONS

This document is a report of the 1985 ERG meeting where the SRP salt irradiation effects program was reviewed; no new tests or experiments were performed for this document. Specific test conditions vary for each experiment and are not covered in this document (see HLW RELATED REPORTS).

METHODS OF DATA COLLECTION/ANALYSIS

This document is a report of the 1985 ERG meeting where the SRP salt irradiation effects program was reviewed; the methods of data collection and analysis are not covered in this document (see HLW RELATED REPORTS).

AMOUNT OF DATA

No new tests or experiments were performed for this document and no data is presented (see HLW RELATED REPORTS).

UNCERTAINTIES IN DATA

The ERG identified uncertainties in the salt irradiation effects database and made recommendations on action which should remove these uncertainties. ONWI's response to each of these items is given in the section of this review DEFICIENCIES/LIMITATIONS IN DATABASE. The uncertainties in the database identified by the ERG are:

1. Experiments on pure single crystals are not relevant to the bedded salt environment and the extent of the damage to the salt structure itself is of little interest.

2. Repository conditions and designs need to be finalized so that testing in representative conditions can begin.

3. Long-term and low-dose-rate tests need to begin now so that the low-dose-rate hypothesis of Levy et al., 1984, can be tested.

4. Investigations need to be integrated.

5. The significance of hydrogen production by irradiation of the brine, oxidation of radiation induced colloidal sodium and oxidation of the steel overpack should be evaluated.

6. Radiolysis will promote oxidizing conditions and corrosion of the steel overpack will promote reducing conditions. The relative significance of these two need to be evaluated.

7. The effects of various reactions on the pH of the environment need to be assessed using the results of ongoing projects.

8. Factors contributing to waste package degradation appear minor based on current design assumptions and knowledge. However, these factors need to be quantified to the extent possible and unanticipated factors identified.

9. To determine the chemical environment at the waste package as a function of time, the SRP needs to (1) place bounds on the colloidal sodium and chlorine production rates, (2) determine the mobility of $Cl_2$ and $H_2$, (3) identify sources of volatile gases in natural salt, (4) compute $H_2$ fugacities and (5) integrate radiation, corrosion and brine migration models.

10. Calculations of the chlorine release at low dose rates need to be performed to indicate whether or not the pH will change significantly and alter the corrosion behavior.

11. Chlorine release rate calculations need to be integrated with brine migration studies.

12. Calculations should be made based on available data to determine the potential impact of colloid formation on brine chemistry.

13. Modeling of coupled subsystems will asses the importance of individual processes.

14. Calculations need to be carried out to indicate whether or not the dose-rate dependence of Levy et al. is of major engineering significance.

15. The effect of higher pH around the waste package needs to be assessed.

16. The effect of chlorine release on corrosion needs to be assessed.

17. A detailed calculation of the effects of stored energy are needed.

18. The amount of colloidal sodium present does not appear significant.

19. To properly assess the effects of irradiation, brine chemistry and corrosion, a suite of realistic scenarios must be invoked and evaluated.

20. Experiments on the mechanical properties of irradiated salt are needed.

21. Compare Levy's F-center formation rate data to those measured by others and available in the literature.

22. Conduct experiments which compare colloid concentration data to TEM examinations.

23. The effect of corrosion and hydrogen embrittlement on the waste package cannot be ascertained at this time and an ERG meeting should be called with experts on steel corrosion and embrittlement present.

DEFICIENCIES/LIMITATIONS IN DATABASE

ONWI responded to each point raised by the ERG and identified the action being taken to eliminate the deficiencies in the salt irradiation effects database which are responsible for these uncertainties. ONWI's response to each point can be summarized as:

1. The testing has been limited to single crystals because of experimental constraints. However, experiments on aggregates have begun which measure the chlorine release. These experiments will be correlated with the measurements of colloidal sodium. In the future, small-angle neutron scattering may be employed to determine colloidal sodium.

2. ONWI agrees with the need to finalize site selection and repository design.

3. While there is potential value in carrying out long-term testing, there is not a pressing need to start them in the near future.

4. ONWI agrees and integration will be taken into account in future plans.

5. ONWI agrees and these factors will be considered in future package analyses.

6. Future testing should resolve this matter.

7. ONWI agrees. The work of Pederson addresses this subject in part (see pertinent documents section).

8. The SRP waste package testing program is directed towards providing a quantification of these and other factors.

9. Current testing and future modeling efforts will address these issues.

10. ONWI agrees. Currently, data are not available; however, results should be available in FY 86.

11. ONWI agrees that, to the extent possible, these calculations should be integrated.

12. ONWI does not anticipate any significant problems of this nature.

13. ONWI agrees and has structured its program accordingly.

14. These calculations have been performed and demonstrate that without a detailed knowledge of the temperature and transport, reliable estimate cannot be obtained.

15. While changing the pH may alter the reaction rate, the total extent of corrosion is limited by stoichemetry and the quantity of brine reaching the container.

16. This will be included in more detailed analyses of the expected waste package environment.

17. The effects of stored energy do not appear significant.

18. ONWI agrees that this is not a significant amount and ONWI feels that this is still a conservatively high estimate. More precise calculations will be carried out in the detailed performance assessment.

19. ONWI agrees.

20. Some experiments on the mechanical properties of salt are planned.

21. So far as known to ONWI, there are no other F-center formation rate measurements to compare to Levy's.

22. TEM provides only qualitative information and cannot be used to obtain concentrations.

23. ONWI agrees with this importance of this meeting and has scheduled a meeting for the fourth quarter of FY 86.

KEYWORDS

review, gamma radiation, chlorine, hydrogen, radiolysis, colloid, salt, corrosion (uniform or general), hydrogen embrittlement, radiation effects

## COMMENTS

The report reviewed here (BMI/ONWI-626) is a report covering a meeting of the ERG where the SRP salt irradiation effects program was reviewed. This report does not present detailed descriptions of the experimental procedures nor is any data formally presented. As a result, these factors cannot be critically reviewed here. In their review of the SRP salt irradiation effects program, the ERG reach two very important conclusions about the overall program. First, they point out that radiation induced changes in the structure and properties of the crystalline salt are not likely to significantly influence container performance for the expected repository conditions. The ERG point out that experiments can be conducted to test this conclusion. Second, the ERG concluded that while the experiments were well designed, the program was structured to address fundamental scientific questions and ignored the applied questions of interest to the program. That is, the program is designed to address fundamental questions about radiation damage in ionic solids while issues concerning container integrity and potential failure modes are ignored.

## RELATED HLW REPORTS


Bergsma, J., R. B. Helmholdt, and R. J. Heijboer, 1985. "Radiation Dose Deposition and Colloid Formation in a Rock Salt Waste Repository," Nuclear Technology, Vol. 71, pp. 597-607.

DOE, see U.S. Department of Energy. Hobbs, L. W., 1973.

"Transmission Electron Microscopy of Defects in Alkali Halide Crystals," Journal de Physique (Paris), Colloque C9-227. Hobbs, L. W., 1975.

"Transmission Electron Microscopy of Extended Defects in Alkali Halide Crystals," Surface and Defect Properties of Solids, Vol. 4, The Chemical Society, London, UK. p. 152. Jockwer, N., 1984.

"Laboratory Investigations on Radiolysis Effects on Rock Salt With Regard to the Disposal of High-Level Radioactive Wastes," in G. L. McVay, ed., Scientific Basis for Nuclear Waste Management VII, Proceedings of a Materials Research Society Symposium, Vol. 26, Elsevier Science Publishing Company, New York, NY, pp. 17-23. Levy, P. W., 1983.

"Radiation Damage Studies on Natural Rock Salt from Various Geological Localities of Interest to the Radioactive Waste Disposal Program. " Nuclear Technology, Vol. 60, pp. 231-243. Levy, P. W., and J. A. Kierstead, 1984.

"Very Rough Preliminary Estimate of the Colloidal Sodium Induced in Rock Salt by Radioactive Waste Canister Radiation," in G. L. Mcvay, ed., Scientific Basis For Nuclear Waste Management VII, Proceedings of a Materials Research Society Symposium, Vol. 26, Elsevier Science Publishing Company, New York, NY, pp. 727-734.

Levy, P. W., J. M. Loman, and J. A. Kierstead, 1984. "Radiation Induced F-Center and Colloid Formation in Synthetic NaCl and Natural Rock Salt: Applications to Radioactive Waste Repositories," Nuclear Instruments and Methods in Physics Research B1, pp. 549-556. Levy, P. W., J. M. Loman, K. J. Swyler, and R. W. Klaffky, 1981.

"Radiation Damage Studies on Synthetic NaCl Crystals and Natural Rock Salt for Radioactive Waste Disposal Applications." On P. L. Hofman, ed., The Technology of High-Level Nuclear Waste Disposal, DOE/TIC-4621, Vol. 1, Technical Information Center, U.S. Department of Energy, Oak Ridge, TN. Panno, S. V., and P. Soo, 1984.

"Potential Effects of Gamma Irradation on the Chemistry and Alkalinity of Brine in High-Level Nuclear Waste Repositories in Rock Salt," Nuclear Technology, Vol. 67, pp. 268-281. Pederson, L. R., 1985.

"Chemical Implications of Heat and Radiation Damage to Rock Salt," in C. M. Jantzen, J. A. Stone, and R. C. Ewing, eds., Scientific Basis for Nuclear Waste Management VII, Proceedings of a Materials Research Society Symposium, Vol. 44, Materials Research Society, Pittsburgh, PA, pp. 701-708. U.S. Department of Energy, 1985a.

Mission Plan for the Civilian Radioactive Waste Management Program, DOE/RW-0005, Vols. I and II, Office of Civilian Radioactive Waste Management, Washington, DC. U.S. Department of Energy, 1985b.

Salt Repository Project Technical Progress Report for the Quarter 1 January-31 March, 1985, DOE/CH/10140-03(85-2), Office of Civilian Radioactive Waste Management, Washington, DC. Westinghouse Electric Corporation, 1983.

Engineered Waste Package Conceptual Design: Defense High-Level Waste (Form 1), Commercial High-Level Waste (Form 1), and Spent Fuel (Form 2) Disposal in Salt, ONWI-438, prepared for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, OH. Westinghouse Electric Corporation, 1986.

Waste Package Reference Conceptual Designs for a Repository in Salt, BMI/ONWI-517, prepared for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, OH.

APPLICABILITY TO LICENSING
[Ranking: Key Data ( ), Supporting Data (x)]

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

This report is related to issue 2.1.3.1 involving how the chemical characteristics of the brine reaching the waste package container will be affected by radiolysis.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data

Pacific Northwest Laboratory, Richland, Washington 99352

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

Westerman, R. E., Haberman, J. H., Pitman, S. G., and J. S. Perrin, "Corrosion of Iron-Base Waste Package Container Materials in Salt Environments," PNL-SA-14029, March 1986

DATE REVIEWED: 6/22/87; Revised 7/31/87

## TYPE OF DATA

Experimental, general corrosion

## MATERIALS/COMPONENTS

Cast ASTM A-216 mild steel, grade WCA (candidate waste package material)

## TEST CONDITIONS

Steel tested as-cast, homogenized (long-term austenization -- 930°C/24 h/AC)) and normalized (short-term austenization -- 930°C/1 h/AC).

Casting size: 160 kg with minimum dimension of 120 mm (Ref. 1)

Specimen size: 15mm x 15mm x 1.5mm (as machined)

Aqueous environments: Bulk of data from tests reported conducted in brine/water (moist salt). Two synthetic Permian Basin brines used the following solutions: (1) dissolution of salt horizon cores & (2) high $Mg^{++}$ "inclusion brine". Moist salt prepared from dried synthetic salt horizon brine with 20 weight percent synthetic inclusion brine added to provide solid salt/brine mixture. Single test reported for unrefreshed autoclave exposure in synthetic salt horizon brine. Specimens exposed in sealed cans at 150°C. Maximum test period was 12 months.

## DATA COLLECTION/ANALYSIS

Corrosion rates based on weight-loss measurment after descaling with formaldehyde-inhibited HCl. Analysis of corrosion products by X-Ray diffraction and chemical analysis.

## AMOUNT OF DATA

Data presented are summarized from the tables and figures, as follows:

Two tables:

1. Composition of a singled casting Steel Tested (element, weight %)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.25 | Mn | 0.71 | Si | 0.45 | Cr | 0.41 |
| Ni | 0.23 | Cu | 0.14 | S | 0.018 | Fe | balance |

2. Compositions of Synthetic Brines (ion, concentration mg/l))

| ion | synthetic salt horizon | synthetic inclusion brine |
|---|---|---|
| $Na^+$ | 123,000 | 23,000 |
| $Ca^{2+}$ | 1,600 | 15,000 |
| $Mg^{2+}$ | 130 | 53,000 |
| $K^+$ | 40 | 10,000 |
| $Cl^-$ | 191,000 | 210,000 |
| $SO_4$ | 3,200 | 160 |
| $HCO_3$ | 30 | - |
| $Br^-$ | 32 | 2,400 |

Four figures:

(1) total penetration of as-cast steel in moist salt tests:
0 to 12 months, 0 to 0.5 mm penetration

(2) corrosion rates of as-cast steel in moist salt tests:
0 to 12 months, o to 1.0 mm/y

(3) composition of corrosion products from 12 month moist-salt test - Cl, Fe, $H_2O$, Na, Mg - 0 to 40 weight % on dry weight basis

(4) microstructures of as-cast and normalized steel.

## UNCERTAINTIES IN DATA

Author describes test conditions as "severe and conservative" with unlimited quantities of reactants.

DEFICIENCIES/LIMITATIONS IN DATABASE

None stated by author.

KEYWORDS

experimental data, supporting data, corrosion, x-ray diffraction, weight change, simulated field, brine, brine (high ionic content), brine (low ionic content), Cl, Mg, high temperature, static (no flow), cast mild steel, A216 Grade WCA, cast, austenitized, homogenized, normalized, corrosion (general), corrosion (pitting)

COMMENTS

Paper quantifies several important factors affecting corrosion of cast steel in brine environments including:

(1) significantly higher corrosion rates observed in brines containing 53,000 mg/l Mg as compared with low Mg (130 mg/l) brines,

(2) austenizing heat treatment (normalization or homogenization) can reduce corrosion resistance of cast steel, a factor which must be considered when assessing microstructural changes due to weld closures or specified casting heat treatments to optimize mechanical properties.

(3) presence of solid brine phase is not necessary for high corrosion rates to be occur.

(4) corrosion rates decrease rapidly over the initial 12 months of exposure reflecting corrosion product buildup

(5) pitting rates in moist salt are similar to average penetration rates based on weight losses

Authors assume no effect of irradiation on corrosion rate citing previous report (Ref.1). Authors do not address potential effects of $H_2$ pressure buildup in sealed containers in reducing cathodic reactions. Changing corrosion rate with exposure time and environmental fluctuation is a key factor needing further study to assure valid extrapolations to longer term exposures and anticipated environmental variations. More detailed studies of corrosion product formation, structure and retention would be particularly useful. The experiments described in this report assume canisters will be subject to constant environment. Potential effects of alternate wetting and drying or waterline exposure should be considered.

RELATED HLW REPORTS

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

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

(a) Relationship to Waste Package Performance Issues Already Identified

ISTP Issue 2.2.4.1 What are the rates of corrosion as a function of time for the various corrosion modes of the waste package container.

ISTP Issue 2.4 How and at what rates will radionucides migrate through failed waste package.

(b) New Licensing Issues

(c) General Comments

WASTE PACKAGE DATA REVIEW

DATA SOURCE:

(a) Organization Producing Data

Brookhaven National Laboratory, Upton, New York 11973

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

Levy, P. W. and Kierstad, J. A., "Very Rough Preliminary Estimate of the Colloidal Sodium Induced in Rock Salt by Radioactive Waste Canister Radiation", Mat. Res. Soc. Symp. Proc., Vol 26 (1984) p. 727-734, Elsevier Science Publ. Co., Inc.

DATE REVIEWED: 12/31/86; Revised 5/22/87

TYPE OF DATA

Model calculation of interaction of gamma radiation with rock salt leading to formation of colloidal sodium.

MATERIALS/COMPONENTS

Rock salt, gamma radiation

TEST CONDITIONS

Not applicable

METHODS OF DATA COLLECTION/ANALYSIS

Not Applicable.

AMOUNT OF DATA

Figure 1. Typical Canister configuration, cocoon approximation and dimensions used for computations; Figure 2. Radiation Induced Colloid Growth Curves used for computations, absorption coefficient ($cm^{-1}$) vs. total dose,(Mrad); Figure 3. Salt converted to Na colloid (percent) vs. time (years) after emplacement for each layer of surrounding canister; Figure 4. Total colloid mass (kg) in each layer vs. time (yrs) after emplacement; Figure 5. Percent salt converted to colloid vs. distance (cm) into salt for 50, 100, 150 and 300 years after placement; Figure 6. Total colloid mass (kg) in the first 25 cm surrounding the canister vs. time after emplacement; Table 1. Properties of the four waste canisters used to estimate the radiation induced Na (sodium) colloid expected in rock salt adjacent to emplaced canisters (includes dimensions of canisters, air gap, thickness of carbon steel and other overpacks, active length, overpack length, distance

from waste centerline to salt, initial heat load, and initial radioactivity); Table 2. Total mass in kg, of radiation induced Na metal produced in natural rock salt from the WIPP site by gamma-ray radiation from the four canisters described in table 1 at various times after emplacement.

UNCERTAINTIES IN DATA

The authors state that the estimates are based on minimal data and require a large number of assumptions and extrapolations.

DEFICIENCIES/LIMITATIONS IN DATABASE

The authors state that "These estimates are based on minimal data and require a large number of assumptions and extrapolations. For better radiation damage estimates , particularly of the Na metal colloid formed in repository rock salt, improved data are essential."

KEY WORDS

brine, colloidal sodium in SRP, gamma radiation field, laboratory, model for radiation damage of rock salt, radiation damage of rock salt, salt, theory

COMMENTS

This report discusses model calculations involving the formation of a sodium colloid formed in the vicinity of waste canisters in a SRP Nuclear Waste Repository.

Although the authors consider the calculations as crude, the basic contention is that the formation of massive colloids of sodium in the vicinity of the canisters will eventually react with brine to form sodium hydroxide which will drastically change the pH of the local environment. The most important question involves the fate of chlorine formed as a result of radiation of the rock salt. The reviewer does not consider it likely that large amounts of a reactive gas like chlorine will escape from the local environment. More likely, reaction with brine will occur with the formation of HOCl or similar chloric acids which should react with and neutralize the sodium. But more definitive data on the fate of chlorine needs to be obtained.

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

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

This report is related to issue 2.1.3.1 involving how the chemical characteristics of the brine reaching the waste package container will be affected by radiolysis.

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data

Vitreous State Laboratory, The Catholic University of America, Washington, D. C.

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

X. Feng, R. Adiga, A. Barkatt, A. Barkatt, W. Freeborn, P. Macedo, R. Mohr, C. Montrose, R. Mowad, E. Saad, and W. Sousanpour, "Effects of Composition On the Leach Behavior of West Valley HLW Glasses," September 1986

DATE REVIEWED: 4/21/87

## TYPE OF DATA

Experimental data on glass leaching.
Measured viscosities at 1100°C.

## MATERIALS/COMPONENTS

West Valley Demonstration Project reference glass WV-205 and 18 other compositional variants were studied. Six of the glasses contained radiocactive uranium (0.5-1.0 weight percent $UO_2$) and thorium (3.2-3.6 weight percent $ThO_2$); the remainder contained Al and Zr surrogates.

## TEST CONDITIONS

The 4-gram glass samples were ground into -100/+200 mesh powders. A static powder leach test (modified MCC-3 test) was used. The leaching environment was 40 mls of deionized water at T = 90°C.

## METHODS OF DATA COLLECTION/ANALYSIS

Leaching Experiments:

Leachate concentrations were analyzed at 7 and 28 days. Dissolved boron was used to indicate the extent of glass dissolution. Boron concentration in leachant was plotted vs. reduced composition variable (referenced to WV-205 glass). No procedures were specified for determining viscosity.

AMOUNT OF DATA

Data presented are summarized in two tables and one figure, as follows:

Two tables:
1. Compositions of WV-205 and Derivative Glasses.
2. Powder Leach Test Results and Viscosities for WV-205 and Derivative Glasses.

One figure:
1. Concentration of boron in leachant for modified MCC-3 leach tests plotted as a function of the reduced composition variable. (Ordinate: boron concentration, mg/l. Abscissa: reduced composition variable, wt%.)

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

In the abstract, the authors state that the conclusion that glass durability can be expressed as a function of a single reduced composition variable is valid for the narrow glass composition range studied and as long as the pH of the leachate remains nearly constant.

KEYWORDS

data analysis, experimental data, laboratory, deionized, high temperature, static (no flow), 90°C (leaching), borosilicate glass, U, Th, viscosity, leaching

COMMENTS

Corrosion resistance and processability are two of the primary criteria for nuclear waste glasses. Modifying the composition of borosilicate waste glasses to improve one of these properties generally has an adverse effect on the other. The present work attempts to show that certain compositional changes increase durability more than they degrade processability, i.e., increase viscosity. Specifically, aluminum is cited as being somewhat more effective in increasing durability than in increasing viscosity.

The data do in fact indicate that several high-aluminum glasses are among the most corrosion resistant, but viscosity data on several of these glasses are absent. As a result, it is doubtful that the conclusion is justified from the data presented. In fact, inspection of Table 2 indicates that the Defense Waste Reference Glass has a better combination of corrosion resistance and viscosity than any of the West Valley glasses, which are the focus of this study. The work does, however, demonstrate that, for the compositional variants in this study, the durability can be related to a single reduced composition variable.

RELATED HLW REPORTS

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

(a) Relationship to Waste Package Performance Issues Already Identified

This document address issues 2.3.2.1.1, which waste form dissolution mechanism or mechanisms are most likely?, 2.3.2.1.2, what are the rates of dissolution associated with the potential waste form dissolution mechanism?, 2.3.2.2, what non-radioactive dissolution products are likely to be produced from the waste form?

(b) New Licensing Issues

(c) General Comments

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data

West Valley Demonstration Project, West Valley, New York

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

L. R. Eisenstatt, "Description of the West Valley Demonstration Project Reference High-Level Waste Form and Canister," Revision 0, WVDP-056, July 28, 1986

**DATE REVIEWED**: 4/20/87

## TYPE OF DATA

Three main data groups are given: 1) Composition, radioactivity, leaching behavior and physical properties of the WVDP High Level Waste form, each primarily on experimental measurements; 2) WVDP HLW canister dimensions, material, fabrication, labeling, and handling, according to present plans; 3) Expected characteristics of canistered waste, based on calculations.

## MATERIALS/COMPONENTS

West Valley 205 glass waste forms that were melted in a full-scale Slurry Fed-Ceramic Melter (SFCM) or laboratory scale melter. Surface finish was either 200 grit as-cut or 600 grit as-polished.

## TEST CONDITIONS

Leaching tests were carried out using MCC-1 tests (90°C deionized water for 28 days, 400 $mm^2$ glass monoliths with S/V = 10/m) and pulsed flow tests (90°C deionized water, 25 percent exchange per week for 12 weeks).

## METHODS OF DATA COLLECTION/ANALYSIS

Methods for chemical and radioactivity analyses were not specified.
Viscosities were determined by beam bending viscometer (annealing range) and rotating spindle viscometer (high temperature).
Heat capacities were determined on differential scanning calorimeter at 20°C per minute.

Mathematical methods were used to calculate expected of canistered waste characteristics.

AMOUNT OF DATA

Twenty-three tables:

1. A. PUREX Insoluble Solids Chemical Composition.
   B. PUREX Solids Fission Products.
2. PUREX Supernatant Chemical Composition.
3. THOREX Waste Chemical Composition.
4. IE-96 Nominal Composition.
5. Glass Formers Added to West Valley HLW to Melt WV-205.
6. Reference 1987 Radionuclide Content (Curies) of West Valley Waste.
7. Composition of WV-205.
8. Reference Radionuclide Content of a Canister of WVDP HLW.
9. Composition of a Nonradioactive Analogue WV-205.
10. WV-205/SFCM MCC-1 Test Results, 200 Grit Cut Finish Specimens.
11. WV-205/SFCM MCC-1 Test Results, 600 Grit Polish Specimens.
12. WV-205/SM MCC-1 Test Results, 200 Grit Cut Finish Specimens.
13. WV-205/SM MCC-1 Test Results, 600 Grit Polish Specimens.
14. WV-205/SFCM Pulsed Flow Test Results.
15. WV-205/SM Pulsed Flow Test Results.
16. WV-205 Glass Physical Property Data: Summary.
17. Annealing Range Viscosity Data: WV-205.
18. High Temperature Viscosity Data.
19. Glass Transition Temperatures.
20. Heat Capacity ($C_p$) of WV-205.
21. Chemical Composition Requirements for Type 304 Stainless Steel.
22. Temperature Distribution in the Canister.
23. Fissionable Material Content of a Canister of WVDP HLW.

Eight figures:

1. West Valley High Level Waste Processing Flow Sheet.
2. Flow Test Results. (Leach rate of DWRG plotted vs. residence time in years.)
3. Viscosity vs. Temperature for WV-205.
4. Linear Thermal Expansion vs. Temperature for WV-205.
5. Heat Capacity vs. Temperature for WV-205.
6. CTS WVNS Canister. (Design drawing.)
7. West Valley High Level Waste Canister Labeling.
8. WVNS Canister Grapple.

UNCERTAINTIES IN DATA

Activities of fission products may vary from Table VI values as follows: U and Pu about 5 percent, Th about 20 percent, and other actinides about 50 percent.
Table VII contains composition ranges for major WV-205

components, based on uncertainties in waste sample analysis and expected waste stream variations.

Ranges of canister radioactivities are given for each radionuclide corresponding to 80-90 percent canister filling. Uncertainty limits are presented with several glass physical properties:

Glass transition temperature: 451.3-494.8°C
Linear expansion coefficient: ±5 percent
Temperature for 100 poise glass viscosity: ±5 percent
Dilatometric softening point of WV-205: ±5°C
Upper and lower annealing points: ±5°C

DEFICIENCIES/LIMITATIONS IN DATABASE

Further glass durability testing needed. Repository groundwater will be added to the test matrix.

KEYWORDS

experimental data, planned work, radioactivity measurements, chemical analysis, differential scanning calorimetry, laboratory, deionized, high temperature, static (no flow), dynamic (flow rate given), stainless steel, 304 stainless steel, cold worked, commercial high level waste (CHLW), borosilicate glass, density, heat capacity, thermal expansion, viscosity, leaching (spent fuel)

COMMENTS

The purpose of this report is to provide information on the West Valley High Level Waste product which is a) useful in dealing with the waste, and (b) required for Waste Acceptance Preliminary Specifications (WAPS). The report does contain a considerable amount of tabulated information on waste form characteristics based on experimental measurements. It is also a good source of summary information on waste canister plans and calculated expected properties of canistered waste. Glass properties discussed include density, viscosity, thermal expansion, and heat capacity. Leaching studies are given without much detail and include data reported elsewhere. As a result, this report is not a primary source of leaching information.

RELATED HLW REPORTS

1. "Waste Acceptance Preliminary Specifications for the West Valley Demonstration Project High-Level Waste Form, Draft for Concurrence," OGR/B-9 (draft), U. S. Department of Energy, Washington, D.C., April 1986.

2. R. G. Baxter, "Description of Defense Waste Processing Facility Reference Waste Form and Canister," DP-1066, Rev. 1, E. I. DuPont de Nemours and Co., Savannah River Plant, Aiken, SC, August 1983.

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

(a) Relationship to Waste Package Performance Issues Already Identified

This document address issues 2.3.1., what the physical, chemical, and mechanical properties of the waste form?, 2.3.2.2, what non-radioactive dissolution products are likely to be produced from the waste form?

(b) New Licensing Issues

(c) General Comments

Draft Copy

# WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Organization Producing Data

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

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

G. C. Wicks, N. E. Bibler, C. M. Jantzen, and M. J. Plodinec, "Repository Simulation Tests," American Ceramic Society Annual Meeting, 1984

DATE REVIEWED: 6/12/87

TYPE OF DATA

Description of repository simulation leaching test methods. Experimental data on glass leaching.

MATERIALS/COMPONENTS

SRP simulated waste glasses (exact type and composition not specified), both non-radioactive and radioactive.

TEST CONDITIONS

The repository simulation test is a static MCC-1 based test, modified so that the primary leaching vessel is made of the host rock (Tuff was used in this experimental study). The leachant was G-4 groundwater at 90°C. Surface are a to volume (SA/V) ratio was 1.0 $cm^{-1}$. The cup also contained a 304L stainless steel sample cage.

METHODS OF DATA COLLECTION/ANALYSIS

Tests were run for periods of 1, 3, and 6 months. Leachates were analyzed after exposure to determine both pH and species extracted from the waste glass and package components. Method of leachate analysis was not specified.

AMOUNT OF DATA

Three tables:

1. Repository Simulation Studies (list of three repository sites).
2. Repository Simulation Test Conditions (see Test Conditions above).
3. Tuff Tests - Phase 1 (pH changes vs. time).

Seven figures:

1. Analyses and Responsibilities (division of responsibilities between SRL and repository designer).
2. Experimental Apparatus.
3. Rock Cups and Waste Glass Samples (photograph).
4. Experimental Unit (photograph).
5. NL (normalized elemental mass loss) of Lithium in J-13 Tuff GW and System (graphed vs. time, 0-6 months).
6. NL (normalized elemental mass loss) of Boron in J-13 Tuff GW and System (graphed vs. time, 0-6 months).
7. NL (Li) for Radioactive vs. Non-Radioactive Tests (J-13 Tuff GW and System) (graphed vs. time, 0-90 days).

UNCERTAINTIES IN DATA

Even with rock samples from adjacent positions within a single core, the leaching behavior may vary significantly. Thus, the results of a few experiments may not give a true indication of the effects of the host rock on glass leaching performance.

DEFICIENCIES/LIMITATIONS IN DATABASE

The number of tests performed thus far under simulated repository conditions is limited, and interpreting the many possible interactions in the system is complex. Determining the concentrations of various species in the leachate is not sufficient to describe the glass behavior if those species can also originate from the host rock or other system components. Accordingly, internal calibrations for the species leached from the host rock are obtained from a separate volume of groundwater outside the host rock cup (i.e., in contact with the cup but not with the glass specimen). Data thus far are limited and more tests are needed to determine applicability of the method. Ultimately, a complete mass balance may necessary.

KEYWORDS

Experimental data, supporting data, simulated field, Yucca Mountain, tuff groundwater, tuff, static, DHLW, leaching

COMMENTS

This paper describes repository simulation tests designed "to assess the performance of SRP waste glass under the most realistic repository conditions that can be obtained in the laboratory." The factors that went into development of the test method are described. Particularly useful is a discussion of the limitations in repository simulation and the ways that they are addressed by the present method. Some limited data are presented from experiments in which the test is used to characterize leaching in tuff host rock.

In the experimental work, the effects of the host rock and canister material were incorporated into the leaching experiment. This procedure represents an advance in laboratory testing of glass leaching over the standard MCC-1 test. The use of actual groundwater as the leachant contributes to the realism of the simulation, although testing in pure water to approximate "worst case" conditions still has merit. Incorporation of groundwater flow into the test, which the authors suggest is possible, would make the test an even better simulation of repository conditions.

The limited experimental data illustrate the test method but have limited applicability. Because the composition of the waste glasses was not specified, the data are useful only for establishing internal consistency and demonstrating that the radioactive and non-radioactive glasses behaved similarly. The preliminary results presented suggest that the buffering action of tuff will stabilize groundwater pH at lower values and thereby retard glass leaching. This critical aspect of work on the tuff and other repositories is being investigated and reported in other papers scheduled for review. Such behavior should be substantiated and quantified with the final candidate waste form, once its composition has been decided.

<u>RELATED HLW REPORTS</u>

<u>APPLICABILITY OF DATA TO LICENSING</u>
[Ranking: key data ( ), supporting data (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

This review address the issue 2.3.2, what is the solubility of the waste form under the range of potential repository conditions? (Tuff primarily)

(b) New Licensing Issues

(c) General Comments

# WASTE PACKAGE DATA REVIEW

## DATA SOURCE

(a) Organization Producing Data

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

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

N. E. Bibler, M. J. Plodinec, G. G. Wicks, and C. M. Jantzen, "Glass Performance in a Geologic Setting," Summer National Meeting of the American Institute of Chemical Engineers, 1986

## DATE REVIEWED: 6/24/87

## TYPE OF DATA

The paper is a literature review of experimental leaching tests and leaching models. The tests reviewed are laboratory and in-situ simulated repository tests.

## MATERIALS/COMPONENTS

Four glass compositions were generally studied in the reviewed work:

1. SRL-165
2. Defense Waste Reference Glass
3. SRL-131
4. Radioactive glass containing waste from SRP Tank 8.

## TEST CONDITIONS

Detailed descriptions of test conditions were not given. In general, tests were conducted under simulated repository conditions, both in the laboratory and in -situ.

## METHODS OF DATA COLLECTION/ANALYSIS

Not applicable - review paper.

## AMOUNT OF DATA

Data presented are summarized in four tables and seven figures:

Four tables:

1. Principal Composition of Typical Glasses Used to Measure Performance of DWPF Glass.
2. Summary of Expected Repository Conditions.
3. Compositions of Groundwater in Potential Repositories.
4. Calculated Release from DWPF Glass in a Saturated Tuff Repository Using the Mass Transfer Model.

Seven figures:

1. Time Dependent Release of B from DWPF Glass (SRL-131) at 90°C in Deionized Water and Three Synthetic Groundwaters. (0 to 750 days, normalized mass loss range 0 to 140 $g/m^2$)
2. Effect of pH (1 to 11) on Silica Dissolution from Simulated DWPF Glass (SRL-131) at 90°C.
3. Dissolution of Cs-137 (0 to 4 $g/m^2$) from Radioactive DWPF Glass at 90°C in Tuff Groundwater in the Presence and Absence of Tuff Rock. (Leach time 0 to 160 days)
4. Time Dependent Release of Li and B from DWPF Glass (SRL-165 Glass) at 90°C in Reduced and Oxic Simulated Basalt and Granite Groundwaters. (0 to 30 day leach periods)
5. Comparison of the Durability of DWPF Glass (SRL-165 Glass and SRL-13 1 Glass) with Basalt Rock and also Other Glasses Based on the Thermodynamic Hydration Model. (Mass loss based on Si, ranging from 0.1 to 1000 gram/$m^2$, plotted vs. free energy of hydration, 10 to -20 kcal/mole)
6. Release of Pu-239 from DWPF Glass (DWRG Glass) in Brine Solution at 90°C. (ppb Pu-239 plotted vs time, 0 to 60 days)
7. Coupling of Glass Performance and Repository Performance Based on the Model of Cheung. Peak Individual Dose Rates Calculated using Release Ra tes for DWPF Glasses Measured under Laboratory or In-situ Conditions. (Limiting individual peak dose rate as fraction of background, $10^{-6}$ to 1, plotted vs glass release rate $10^{-8}$ to $10^{-3}$/y)

UNCERTAINTIES IN DATA

Not applicable - review paper.

DEFICIENCIES/LIMITATIONS IN DATABASE

1. Site-specific properties of the actual repositories need to be determined.
2. Testing is needed using site-specific groundwaters and rock.

3. The role of colloids in repositories containing iron as the waste package overpack is not understood.
4. The effect of radiation on leaching in reducing groundwaters needs to be studied further.
5. Leaching of additional radionuclides in groundwater needs to be studied.

KEYWORDS

Literature review, leaching, simulated field, DHLW

COMMENTS

This paper reviews published studies on Defense Waste Processing Facility (DWPF) glass degradation in simulations of the proposed repository environments. Such studies overcome some of the limitations of similar experiments in which repository conditions are ignored. This is important because the performance of the glass, as the authors point out, can be directly affected by the test method. This question of test methodology and the ability to predict and simulate reposit ory conditions remains a central issue in evaluating studies of glass waste form leaching. A considerable amount of the discussion in this paper concerns test methods.

The specific effects of simulated tuff, salt, basalt, and granite repository environments on waste glass durability comprise the major part of the review. The paper contains a short overview of the effects of solution composition, pH, and pressure. In addition to reviewing experimental data, the paper discusses two models that couple glass leaching with repository conditions. The first model calculates radionuclide migration rates using known equations for mass transfer by convection and diffusion, assuming that groundwater flow is so slow that radionuclide concentrations at the glass surface are controlled by solubility. The second model is similar to the first, except that it calculates individual peak dose rates that would be obtained at the edge of the repository by drinking the groundwater. Both models are shown to predict low radionuclide release rates in repository environments.

The studies reviewed represent a growing body of work which supports the authors' hypothesis that Defense Waste Processing Facility glass will be more durable in the repository than in predictive laboratory tests. It must be recognized, however, that this hypothesis includes the implicit assumption that the repository simulation tests do indeed simulate the (as-yet poorly characterized) repository sites.

While the review is not exhaustive or extremely detailed, it is a well written, clear, useful summary of available data. Furthermore, it presents current thinking on some of the relationships between the repository environment and glass durability, and identifies several areas which must be studied further.

It is interesting to note that the paper points out that the 131-TDS glass, discussed in the paper, is no longer used for testing glass durability. There has been a shift to higher silica glasses to maximize overall glass properties. A considerable amount of the existing data on waste form leaching, and resulting hypotheses on leaching mechanisms, are based on this glass. As a result, it will be necessary to verify that what has been learned is applicable to the new compositions.

RELATED HLW REPORTS

1. "Repository Simulation Tests", G. C. Wicks, N. E. Bibler, C. M. Jantzen, and M. J. Plodinec, American Ceramic Society Annual Meeting, 1984.

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

(a) Relationship to Waste Package Performance Issues Already Identified

This review address issues 2.3, when, how, and at what rate will radionuclides be released from the waste form?, 2.3.2, what is the solubility of the waste form under the range of potential repository conditions?, 2.3.2.1.1, which waste form dissolution mechanism or mechanisms are most likely?, 2.3.2.2, what non-radioactive dissolution products are likely to be produced from the waste form?, 2.3.2.3, what are the solubilities of the radionuclides released from the waste form?, 2.3.2, what colloids or other suspended particles will be produced from the waste form?

(b) New Licensing Issues

(c) General Comments

Appendix B. Database Activities for the NBS/NRC Database for Reviews and Evaluations of High-Level Waste Data

Work on improving the searching capabilities and the speed of searching the Database (for Reviews and Evaluations on High-Level Waste) continued during the six months from February 1987 to July 1987. Enhancements to the software developed during this period are highlighted below.

Various system routines were developed: Items B, C, and D listed below are largely transparent to the user, but these changes enhance efficiency of data handling and retrieval.

Item A -- Help Menus Version 1.0 and 1.1 have been developed. Examples of help menu screens developed at NBS are located in the Monthly Letter Status Report for April 1987 (FIN-A-4171-6). Help menus lead a user through a series of choices. The end result of these choices is a completed search or query. By using the help menus, a novice user of the NRC/NBS database is able to search for information more quickly and easily. In the first test version (1.0) of Help Menus, each time new keywords were added to the database, it was necessary for a systems programmer to update a series of help menu screens. This process has been automated in Version 1.1, so that whenever keywords are added, the information specialist runs a program and the menu system will be updated to merge the new keywords with the older keywords. The new file is reflected immediately in the help screens.

Item B -- Previously, there was no command that would instruct the user on the organization or logic structure of the database. The logic structure of the database is referred to as the database tree. Now, to see how the database is organized, the command DATABASE.TREE produces the current version of the database tree. The database tree is now derived from the structure that exists at the time the command is given. This is important when frequent minor changes are made in the file structure. A tree derived in this way can be printed to the screen or the printer.

Item C -- A command has been added to find empty fields in a file. This command, called FIND.EMPTY, will locate the empty fields in a record and print the field names to either the screen or printer. This is helpful in verification of data entry and in answering a query.

Item D -- The input screen routines for abstracts have been modified. During data entry, if a document does not contain an abstract, the input routine will automatically place the text string, "No abstract.", in the field. This speeds data entry and retrieval.

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