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Review of DOE Waste Package Program

Semiannual Report Covering the Period April 1985 - September 1985

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Prepared for
U.S. Nuclear Regulatory
Commission

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ABSTRACT

Detailed evaluations continued on DOE reports and papers concerned with the evaluation of waste package component behavior. The intent was to estimate the quantity and relevance of data being generated for barrier system performance analysis. In addition, several review studies have been completed to evaluate progress in the DOE waste package program. These include work on the selection of a glass composition for West Valley, New York, high level waste, a description of the system at West Valley for vitrifying the waste, and reviews of papers included in the Defense High-Level Waste Leaching Program and the recent Tucson, Arizona, "Waste Management '85" Conference.

CONTENTS

CONTENTS (Continued)

FIGURES

TABLES

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1.0 INTRODUCTION

The work described in this report is a continuation of the study to review the Department of Energy (DOE) high-level waste package program. It covers two main areas, one monitors the broad DOE strategy for developing acceptable barrier materials, and the other is concerned with the quantity and relevance of the data needed for estimating their long-term performance with respect to NRC requirements.

In the following section of this report is described the effort to conduct detailed reviews of individual reports and publications on DOE waste package evaluation studies. Limitations in the data are specified, together with recommendations for future DOE research to fill gaps in the data base. The reviews are in the format of a Waste Package Data Review Form, which is meant to be compatible with a companion NRC program at the National Bureau of Standards in which waste package materials data is being reviewed and stored in a computer system to facilitate its use in performance evaluation studies for the NRC.

Other sections of the report deal with a review of the studies being carried out to define a reference glass composition for West Valley, New York, high level waste; a critique of work being carried out in the West Valley Demonstration Project; a review of work being performed as part of the Defense High Level Waste Leaching Program, and finally a brief outline of observed inconsistencies in the waste inventory data published in a DOE Environmental Assessment report.

2.0 REVIEW OF DOE WASTE PACKAGE DATA BASE

Appendix A contains a compilation of detailed reviews of recent waste package material studies. These reviews supplement the previously published studies published in this program (NUREG/CR-2482, Vol. 8, 1985).

2.1 Reference

NUREG/CR-2482, Vol. 8, "Review of DOE Waste Package Program, M. S. Davis (Editor), 1985.

3.0 REVIEW OF WEST VALLEY HIGH-LEVEL WASTE GLASS DEVELOPMENT

A review was conducted of a recent PNL report (PNL-4992, 1984) which outlined efforts to specify a reference composition for West Valley high level waste. Independent variation of seven components (SiO_2, B_2O_3, Na_2O, CaO, Al_2O_3, Fe_2O_3, and the other constituents of the West Valley waste called ('waste mix') has been considered in a restricted range within which an optimum composition is to be found. Empirical models of composition dependence of viscosity and electrical conductivity of the melt, and slow-cooled crystallinity and leachability of the glass have been developed for various waste loadings. By defining a narrow range of the process parameters (viz. temperature, viscosity and electrical conductivity) and tendency of the glass to devitrify under a particular heat treatment, a large fraction of possible glass compositions was eliminated from further consideration. The optimum composition (45.4 wt% SiO_2, 2.4 wt% B_2O_3, 15.5 wt% Na_2O, 10.2 wt% CaO, 0.9 wt% Al_2O_3, 13.5 wt% Fe_2O_3, 12.1 wt% waste mix) from the remaining composition range was obtained such that a 'composite leach rate' has the lowest value while waste loading is maximized. Experimental data for more than one hundred glasses specifying the temperature at which the viscosity of the melt is 100 poise, electrical conductivity at that temperature, devitrification as observed by x-ray diffraction, the silicon leach rate under four test conditions and the change in pH of leachant in one test are used in the optimization procedure.

Considering that a high-level waste glass may consist of more than twenty components, it is almost impossible for an optimum composition to be determined from the current knowledge of glass science. Therefore, the statistical modeling procedure adopted in the report is a step in the right direction. However, to reduce the initial computer-generated number of over a million possible glass compositions to approximately one hundred, the authors had to place several constraints on processing parameters and some physical properties of the glass. A large number of these constraints are based on qualitative arguments or somewhat arbitrary assumptions in the absence of any other criteria. It is very likely that the optimum composition would change if these constraints are modified. Specific assumptions which could alter the presently obtained optimum composition, some already identified by the authors themselves, are briefly discussed below:

(1) Processing parameters such as melt viscosity and melt conductivity are considered to be the primary criteria in composition selection. However, for a high-level waste form, leaching should be considered the most important consideration. This may require defining the minimum acceptable leach rates for various radionuclides.

(2) For a glass composition to be admissible for further consideration, its viscosity is required to be 100 poise within the narrow temperature range of 1100-1150°C. While this restriction appears to conform to ordinary glass making procedure, there is nothing special about this range. A correlation had been established in the report (Figure 3.1) which shows that a low 'composite leach measure' is obtained for glasses requiring processing at higher temperatures (therefore, higher cost). It is possible that an increase in cost due to higher melting temperature can be offset by a much improved durability. Therefore, a cost analysis to justify the limits of temperature is warranted.

(3) A viscosity of 100 poise is required so that pouring of glass is easily accomplished. Lower viscosity has been considered unsuitable because the melt then causes excessive refractory corrosion and volatilization of constituents. However, viscosity can be easily increased by decreasing temperature, which a priori does not seem to have any adverse effect.

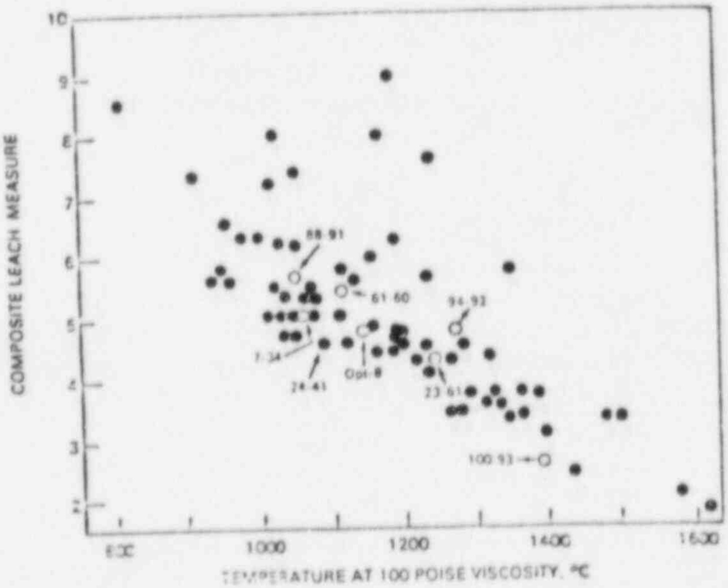

Figure 3.1 Leaching performance versus processing temperature. From PNL-4992.

(4) Exclusion of a glass composition because its viscosity is strongly temperature dependent is a criterion which can be relaxed in some cases by selecting appropriate heating conditions.

(5) Quantitative measurement of crystallinity in a glass by comparing X-ray diffraction integrated intensity with an Al_2O_3 impregnated specimen is an admittedly vague concept; the meaning of negative crystallinity as shown in Figure 3.2 is not clear. Consideration of crystallinity as a primary selection criteria is not very convincing because there is no definite adverse effect of crystallinity on the relevant properties of all the glasses; leach resistance, which may or may not be low in devitrified glasses, is of basic importance.

(6) Crystallinity is included in optimization for slow cooled glasses and measured for a few other heat treatments, but the actual heat treatment in a waste canister is too complex to be represented by simple heat treatments.

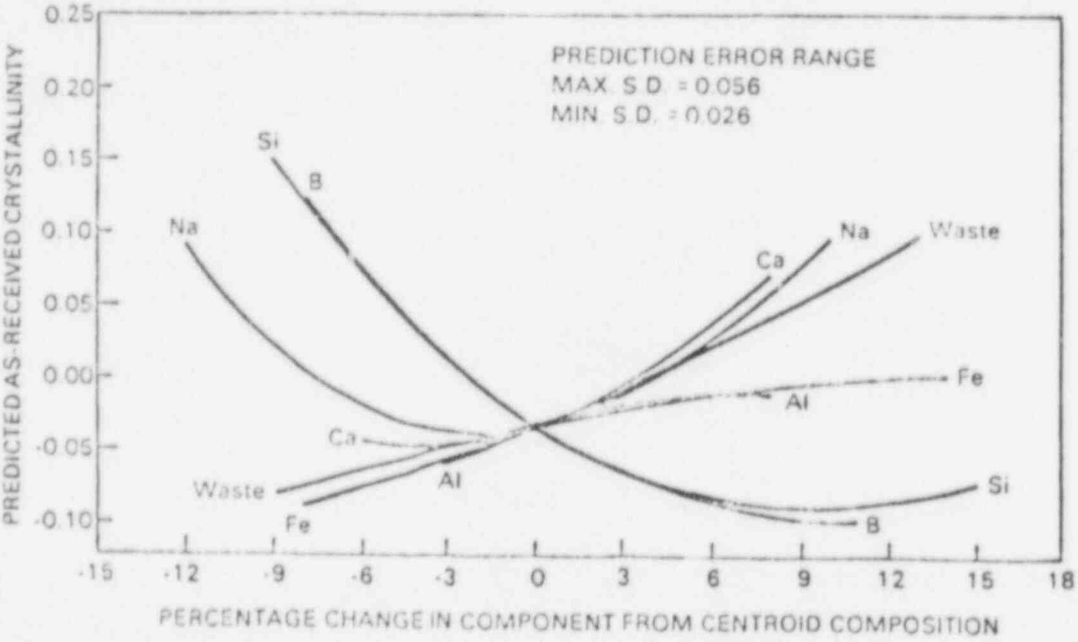

Figure 3.2 Effects of components on as-received crystallinity. From PNL-4992.

(7) 'Composite leach measure' has been defined as the sum of the logarithm of the Si concentration under four test conditions using MCC-1, MCC-2 and MCC-5 tests, and pH of leachant in an MCC-3 test. It is used as the criterion for leaching tendency of a glass composition. However, it is well known that leaching of a waste glass is too complex a phenomenon to be quantified by results from such arbitrarily defined tests.

The 'composite leach measure' should be considered only as a very crude guideline because the tests are conducted under highly simplified conditions e.g. a test duration of 3-28 days, or use of deionized water, has little resemblance to repository conditions. Furthermore, no testing is conducted in high pH or Eh conditions which can be present under certain repository performance scenarios, and all emphasis is placed on the leaching of silicon.

(8) Selection of a leach test appears to be important in determining the effect of various constituents in the glass. For example, variation of iron concentration in glass shows a minimum in silicon leach rate at the centroid composition only in one of the tests (Figure 3.3) but not in others (e.g. Figure 3.4). Thus, the optimum composition appears to depend on details of the leach test. The authors consider the flowing leach test more appropriate for repository conditions but exclude it for economic reasons.

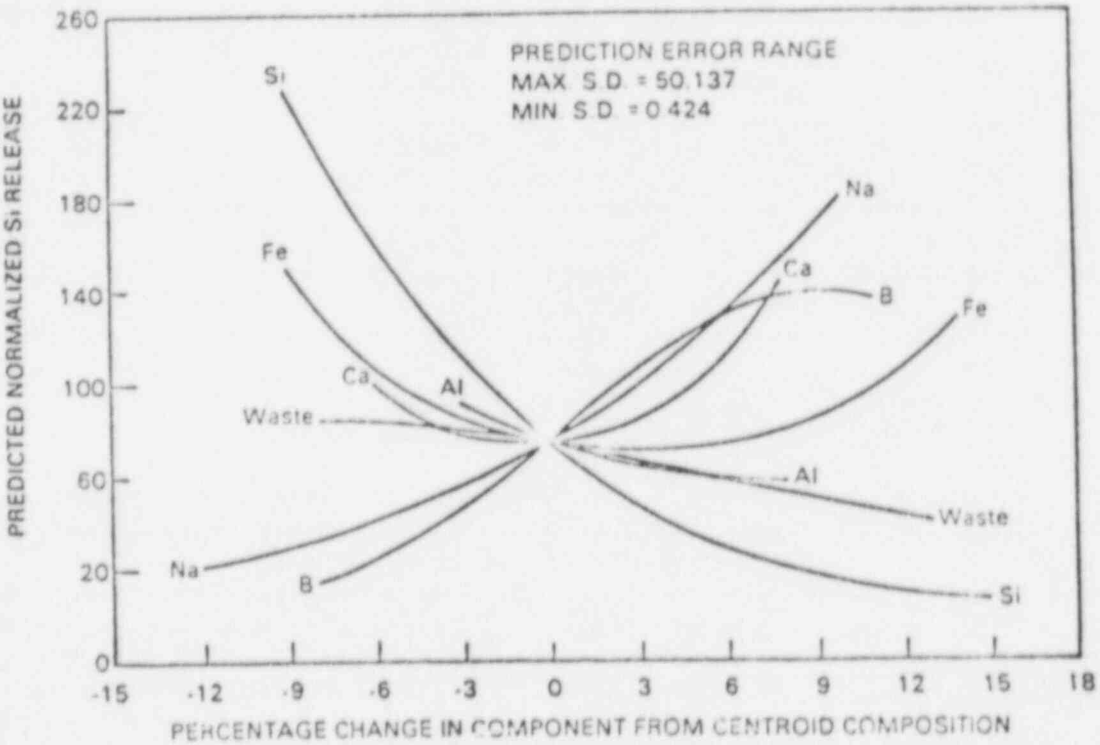

Figure 3.3 Effects of components on predicted normalized Si release for Test 3 (7-day, 90°C, SA/V = 2 m^{-1}, pH 3 buffered solution). From PNL-4992.

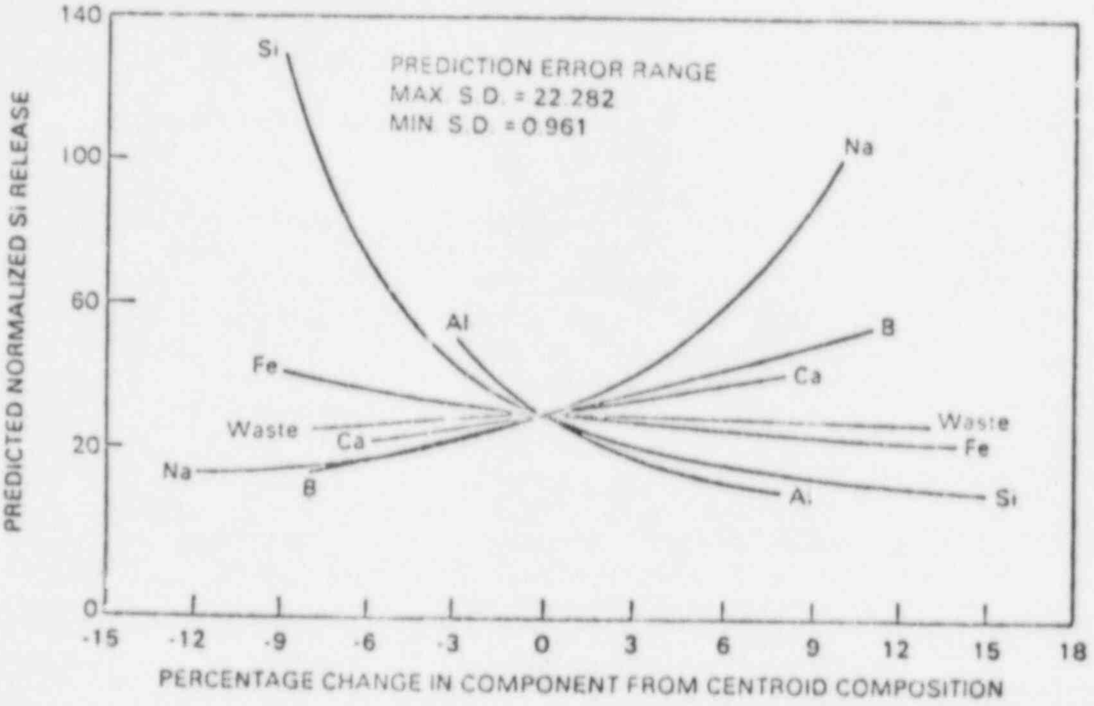

Figure 3.4 Effects of components on predicted normalized Si release for Test 1 (7-day, 90°C, SA/V = 2 m^{-1}). From PNL-4992.

(9) The electrical conductivity of the melt is important for electrical heating. In the optimization procedure its value at 100 poise viscosity is required to be 0.15 to 0.50 $ohm^{-1}cm^{-1}$. However, conductivity is important not just at one particular viscosity value but for the complete range of operational temperatures. An upper limit is assigned to conductivity (0.50 ohm^{-1} cm^{-1}) so that excessive electrode deterioration under high current density does not occur. In case of such a possibility, the current density can be reduced by decreasing the applied potential.

In summary, the procedure developed in the report, to statistically design an optimum glass composition, is an acceptable approach to the problem at this time. However, several compromising assumptions have been made to limit the number of experiments, or because appropriate guidelines on waste form performance are not available. It is possible that when additional and more repository-relevant data become available, a significantly different optimum composition than predicted in the present report will be obtained.

4.0 REVIEW OF PROJECT PLAN FOR THE WEST VALLEY DEMONSTRATION PROJECT

A copy of the Project Plan was requested from the West Valley Demonstration Project (WVDP) Office, New York, and it was received in March.The report (not numbered) generally describes the plan to immobilize high and low level wastes at West Valley, and to decontaminate and decommission the facilities used. The report may be a little dated since it refers to work that will be performed although the completion dates have already passed. Nevertheless, the contents of the Project Plan are of value since in certain cases it describes the types and schedules of formal interactions with NRC. Recent discussions by the writer and WVDP staff indicate that the Project is on, or ahead of, schedule. Below is given a general review of the subject report prepared by the WVDP staff.

4.1 Introduction

In 1980, Congress passed Public Law 96-368, which is the West Valley Demonstration Project Act. The law authorizes DOE to solidify the high level wastes at West Valley into a form that can be transported to, and disposed of in, a Federal repository. The work will be funded 90 percent by DOE and 10 percent by New York State.

The report states that the overall approach to the Project is to make maximum use of existing technology; minimize new development; proceed quickly with innovative engineering solutions and design for specific systems and components; and to proceed to commit to hardware on more clearly defined tasks while designing other portions of the systems. Although it was recognized that this could lead to an occasional retrofit and delay, it was thought to represent a less expensive strategy since it would shorten the overall task.

Figure 4.1, prepared in 1984, shows the work and schedules for the Project. It is divided into six subtasks with vitrification commencing at the beginning of fiscal year 1989. Also included in the schedule are the delivery dates of various volumes of the Safety Analysis Report (SAR) to the NRC.

In the sections below, selected aspects of the WVDP report will be discussed.

4.2 Type of Waste at West Valley

The Project Plan briefly describes the contents of the two high-level waste tanks. Tank 8D2 contains about 560,000 gallons (2.12 million liters) of PUREX waste. Over 90 percent is supernatant liquid containing about 90 weight percent of dissolved sodium salts (nitrate, carbonate, sulfate) and about one-half of the total radioactivity in the form of cesium salts. Only small amounts of strontium are dissolved in the supernate together with small amounts of plutonium as fine particulates. The remaining 10 percent of the waste volume is in the form of a sludge containing the other half of the radioactivity in the form of fission product metal salts (nitrates, carbonates, hydroxides and oxides). Strontium salts are the main constituents of the sludge with lesser amounts of other fission products and actinides.

PROJECT SCHEDULE - 1984

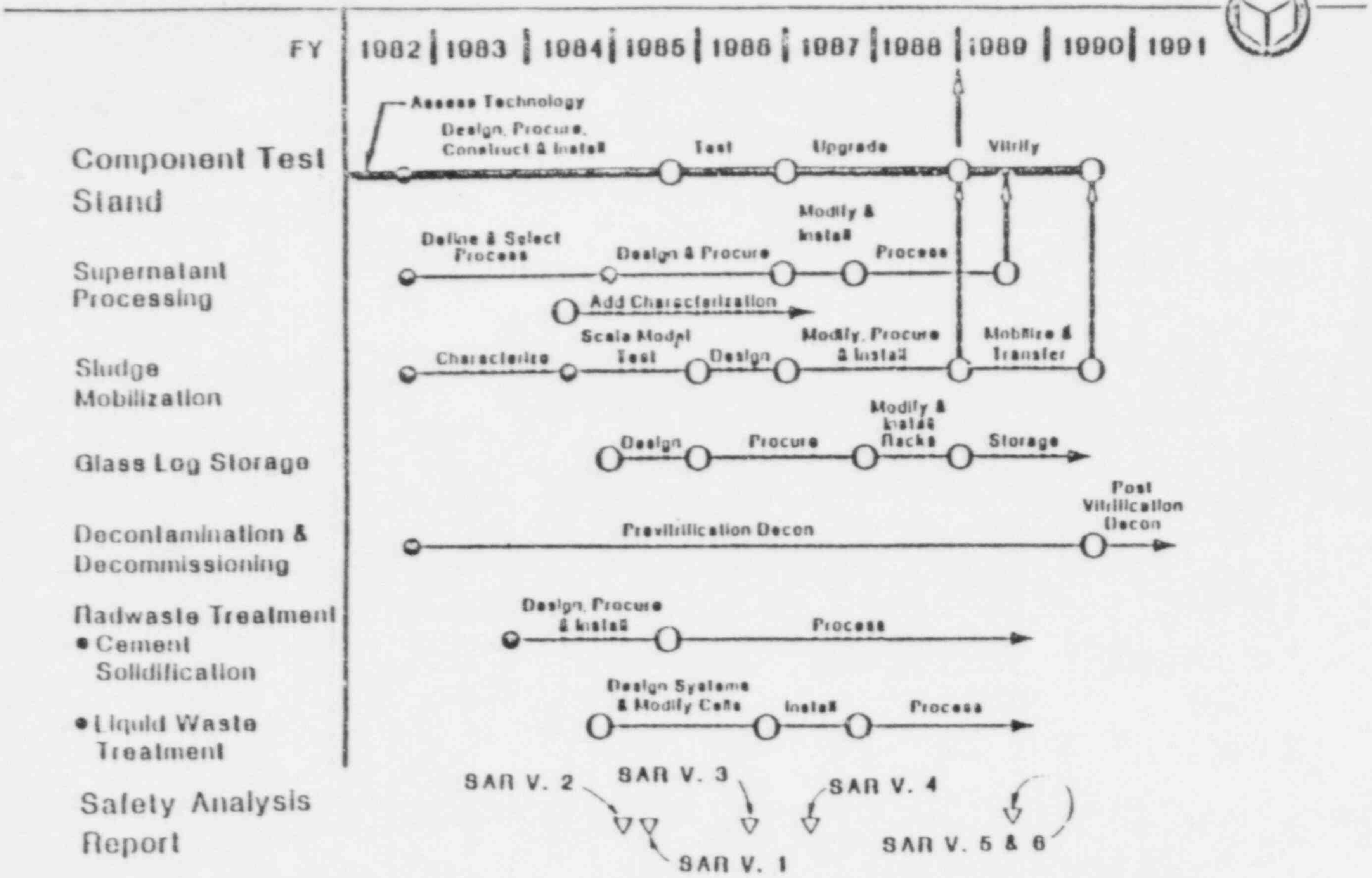

Figure 4.1 Project schedule.

Earlier reports frequently cite the waste in Tank 8D2 as being "neutralized" from an initial acidic condition, to protect the steel tanks from corrosion. The Project Plan, however, states that the supernate is alkaline. This writer contacted the WVDP office and was told that, in fact, the waste was not neutralized but made alkaline. The pH of the solution is about 10.

4.3 Vitrification of HLW

Work will involve cleaning the supernate by passing through zeolite ion-exchange columns. The sludge will be washed to remove excess sodium salts and the wash water also cleaned by passing through zeolite columns. The sludge, the loaded zeolites, and controlled amounts of acidic THOREX waste from Tank 8D-4 will be blended and vitrified in a Joule-heated, slurry-fed, ceramic melter. According to information obtained by the writer from the WVDP, several candidate glass compositions have been identified for continued study. A recent study by Chick et al., (PNL-4992, October 1984) which statistically determined an optimum composition based on glass-property and processing factors probably helped to identify the WVDP glass compositions. Chick's optimum composition is 45.4 wt.% SiO_2, 2.4 wt.% B_2O_3, 15.5 wt.% Na_2O, 10.2 wt.% CaO, 0.9 wt.% Al_2O_3, 13.5 wt.% Fe_2O_3, 12.1 wt.% waste mix. The PNL report has been reviewed by BNL and the findings are given in Section 3, above.

Three important technical problems currently exist with respect to preparing a homogenized feed from the waste tanks to the vitrification facility:

a) An agreement between DOE and NRC states that "the largest volume of HLW contained in one tank (8D-2) cannot exceed the operating volume of the spare tank." This limits the amount of liquid that can be added to Tank 8D-2 for sluicing, (sluicing is the procedure for mechanically agitating, breaking and mixing the settled sludge).

b) Only two risers in Tank 8D-2 are sufficiently large to accomodate sluicing equipment and about 3-4 will be required to complete the job.

c) Sluicing will be difficult because of the network of grids at the bottom of the tanks.

To resolve the above problems a 1/6 scale model of Tank 8D-2 was constructed together with a 1/6 scale low pressure sluicer to estimate behavior of a full-size system. A similar system was previously constructed and operated successfully at SRL. The WVDP test program on sluicing will be developed through meetings with SRL and RHO staff.

4.4 Storage and Transportation of HLW

The glass will be poured into containers (material not given) which will be 0.61m in diameter by 3m in height. About 300 glass logs will be produced, and these will be dry stored in a process cell until they can be shipped to a Federal repository. An SNL shipping cask is under study for this purpose.

4.5 Other Types of Waste

Waste generated from plant maintainance, vitrification, and decontamination activities include low-level and transuranic wastes. Solid LLW will be compacted and packaged in drums or rectangular steel boxes. Larger contaminated equipment will be decontaminated to a level deemed safe for on-site handling and prepared for disposal.

For wet low-level and transuranic waste, a system is being prepared to encapsulate items in cement. The transuranic waste will be disposed of in a Federal facility. Figure 4.2 is a process flow chart for the WVDP waste isolation system.

4.6 Decontamination and Decommissioning

The Project Plan very generally describes how existing facilities at West Valley may be decontaminated and prepared for integration into the vitrification program, and how post-operational decontamination and decommissioning will be carried out. There is virtually no technical information in the report except to state what techniques will be used to accomplish particular tasks. The Plan states that a post operation "Project Decommissioning Plan" will be submitted to the NRC and that "the NRC, consulting with other affected or interested parties will determine the decontamination requirements."

4.7 Safety Analysis Reports

A Safety Analysis Report will be prepared by WVDP to assess the risk to public health and safety from Project activities. Table 4.1 describes the individual volumes in the SAR and their dates of submission to the NRC. Each volume will cover the following topics:

- Description and evaluation of the project facility or process;
- Design criteria for systems, components and structures;
- Normal and emergency operating procedures to be used;
- Identification of hazards;
- Physical design features and administrative controls provided to prevent or mitigate potential accidents;

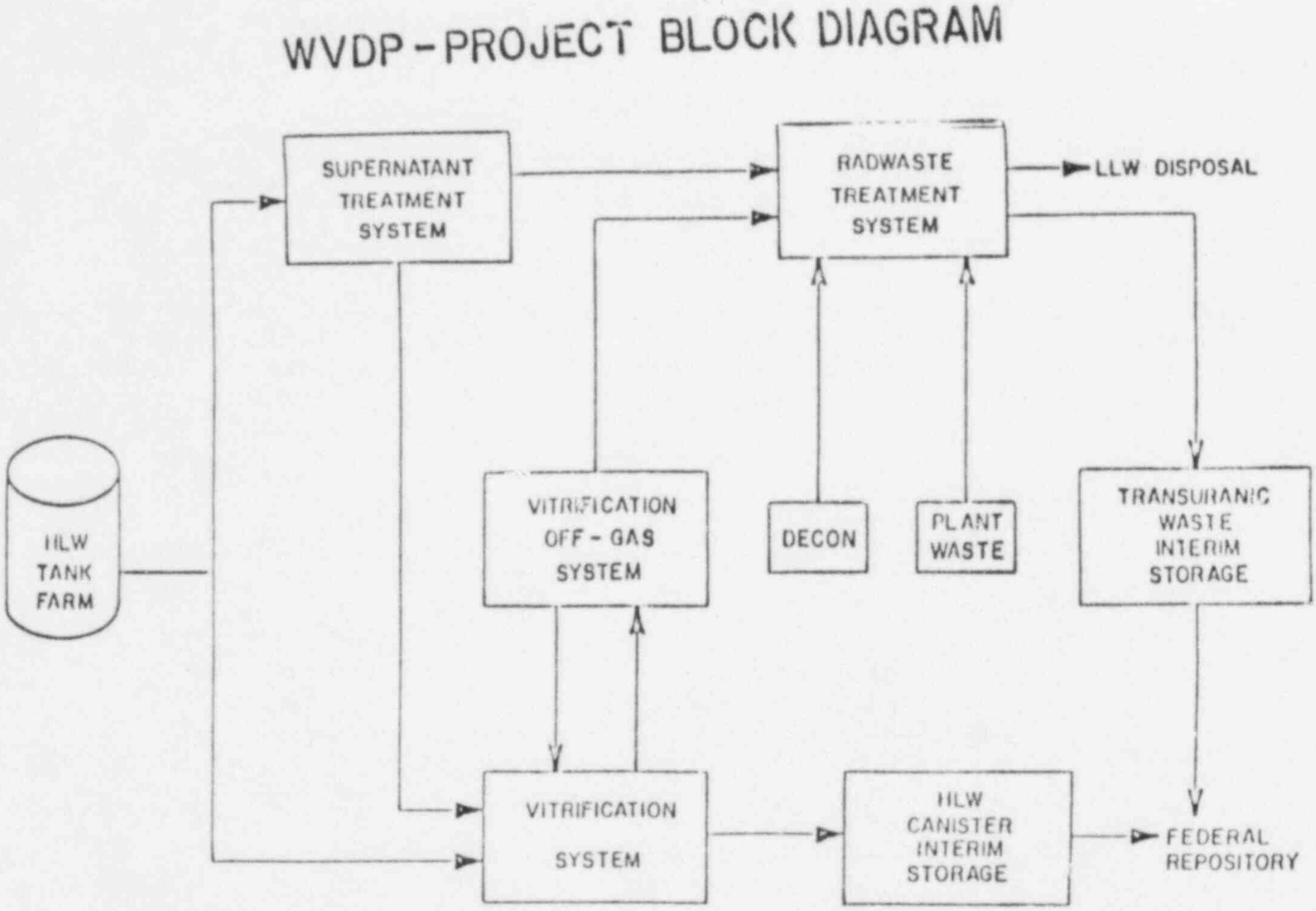

Figure 4.2 WVDP - project block diagram.

- Potential accidents and consequences including those resulting from natural phenomena;

- Operational limitations; and

- Means for controlling effluents and minimizing radiation exposure.

The WVDP staff feels that a staggered issuance of the SAR volumes is reasonable since different parts of the plant are scheduled for completion at different times. However, this strategy could create certain problems since it is unlikely that the safety of all subsystems of the facility can be assessed in isolation. In other words, the safety of a system cannot be accurately evaluated until those of related systems are also defined. Thus, the NRC should determine whether the sequential preparation of individual volumes of the SAR is appropriate. A possible compromise would be the issuance of a complete (if abbreviated) preliminary SAR. Timely response by NRC to this document could help limit some of the costly retrofitting of systems that the WVDP staff considers to be a possibility in the program.

4.8 Summary

The version of the Project Plan (Rev. 0) for the WVDP which was reviewed here appears to be a little dated. It was not very well prepared since some figures were barely legible and they were frequently cited and placed randomly in the report. There was, however, enough general information to follow the overall plan of activities but there was a complete lack of reference to supporting documents that could be used to define some of the detailed technical work that will be needed.

It is felt that the NRC should remain aware of the following items as the WVDP proceeds:

- The glass waste form is still under active development - no specific composition has been defined by the WVDP and, thus, no significant data base is available on leachability at this time. The "optimum" composition cited by PNL may not be the one finally selected.

- The pour container material for the glass was not specified. Since the container will have a potential for containing the enclosed radionuclides, the choice of material should be stated so that its effect on the containment time can be evaluated.

- The strategy to order and install hardware, while designing other parts of the waste solidification system, must be viewed with caution. It is possible that an early commitment to a particular item of hardware, especially if it is costly, may preclude its modification or replacement later. Thus, the overall system may be compromised in terms of performance and safety. It seems clear from the report that schedule and cost are two of the most important criteria in the WVDP program.

Table 4.1 Structure of the West Valley Demonstration Project safety analysis report.

Volume	Title	To NRC Schedule Date by Quarter
I	Project Overview and General Information	2nd of FY 1985
II	Existing Plant and Operations	1st of FY 1985
III	High-Level Waste Vitrification	
	• CTS Cold Operations	4th of FY 1985
	• Vitrification Facility (PSAR)	4th of FY 1985
	• Supernatant Treatment System	3rd of FY 1985
	• Sludge Mobilization System	3rd of FY 1986
IV	Waste Management, Storage and Disposal	
	• Vitrified High-Level Waste Storage	2nd of FY 1987
	• Cement Solidification System	2nd of FY 1985
	• Liquid Waste Treatment System Upgrades	1st of FY 1986
	• Size Reduction Facility	Open
	• Disposal Area Operations	4th of FY 1985
V	Final Decontamination, Decommissioning and Waste Shipment	3rd of FY 1989
VI	Operational Safety Requirements (Technical Specifications)	Concurrent with each section

- Detailed technical descriptions of the program are not necessary in a Project Plan, but references to such work would be useful for those reviewing the WVDP in detail.

- An early Preliminary SAR would be very useful to NRC since it would scope out the safety of the whole WVDP effort. The current plan to issue the SAR over a period of about four years could lead to difficulties in assessing and correcting safety issues associated with separate Project systems.

5.0 REVIEW OF THE DEFENSE HIGH-LEVEL WASTE LEACHING PROGRAM

5.1 Introduction

The Defense High-Level Waste Leaching Mechanisms Program was a three-year study by two National Laboratories (PNL and LLNL), one industrial laboratory (Rockwell Science Center), and three universities (Catholic, Penn State, and Florida). The objective of this study was to determine the dominant leaching mechanisms for proposed borosilicate defense waste glasses and to evaluate the effects of some major environmental parameters (groundwater composition, flow rate, temperature, pH, Eh, radiation field, and presence of ductile iron or basalt in the leachant) upon leaching mechanisms. A final report describing the output of the study has been completed (PNL-5157, 1984) and this is reviewed below.

This report is comprised of seven chapters and three appendices, each dealing with a different aspect of leaching. The first chapter is preceded by a summary and conclusion section which presents the major results obtained from this study. Below is given a brief description of each chapter and a discussion of questions left unanswered by the results of the leaching mechanisms program. This will be followed by a summary of comments on the report.

5.2 Mechanisms of Defense Waste Glass Corrosion: Dissolution of Glass Matrix

This chapter presented a detailed state-of-the-art discussion on leaching of TDS-131 and Defense Waste Reference Glass (DWRG) in deionized water at temperatures ranging from 40-90°C, a variety of flow rates ranging from zero flow to roughly 100 mL/hr, and a range of waste form surface areas to solution volume ratios. A few studies were conducted using groundwaters that simulated expected repository conditions.

The major conclusions reached in this section of the report were concerned with leaching of a waste glass as a function of flow rate, and are as follows:

a) At low flow rates the release rate is directly proportional to the flow rate.

b) At high flow rates the release rate is nearly independent of flow rate and depends on the kinetics of glass dissolution.

c) At low flow rates the solution concentration of some elements (Si in particular) is controlled by saturation limits with respect to the hydrated layer of the glass. This leads to surface alterations as species precipitate on the glass. These alterations form a barrier to further release from the glass, which retards the release of all glass species, even those that are not saturation-limited. It should be noted that the interpretation of the barrier as a protective layer is subject to much debate. While everyone agrees that the formation of precipitates in the gel layer leads to reduced leaching of all glass components, many people believe that this is due to solubility constraints between the gel layer and bulk glass which prevent further breakdown of the glass network, whereas this study interprets the precipitates as forming a barrier to migration of species from the bulk glass to the porous hydrated layer and eventually into solution. These interpretations can lead to significantly different long term predictions. The protective layer theory will predict zero release if the layer prevents migration to solution. However, the solubility controlled release model allows for a continual breakdown of the glass network and concomitant release of all species to replace saturated species lost due to the replenishment of solution owing to flow.

d) DWRG is much more durable than TDS-131 under expected leaching conditions. This is due to the higher silica and lower soda content of DWRG compared to TDS-131. The higher silica content decreases the pH rise that occurs with leaching. This is particularly important in slow flow or static tests which allow the pH to increase more than high flow rate tests. It should be recognized that DWRG is similar in composition to SRL-165 glass, which is a primary candidate for the defense glass composition.

e) At high flow rates the glass leach rate is dependent on glass surface area; at low flow rates solubility controls become important and the leach rate is independent of glass surface area. Thus, at the low flow rates expected in a repository it is unimportant if the glass fractures, exposing a large surface area.

f) Tests in silicate groundwaters indicate that leaching is reduced when compared to leaching in deionized water.

g) These tests "indicate that matrix dissolution at high flow rates and pH-dependent saturation with respect to silica and alumina and reprecipitation at low flow rates are the major mechanisms controlling glass dissolution."

Over the range of parameters tested, this chapter presents a tremendous quantity of leaching data. It should be recognized that over one-half of the data has been obtained for TDS-131 glass, which is not under consideration for use in the final disposal scheme and, therefore, these data are not directly applicable to demonstration of compliance with regulatory criteria. Also, although DWRG is close to the favored composition for defense waste glass, these tests were conducted without any waste and, therefore, no radiation field. The influence of radiation is considered in another chapter. In any case, the mechanisms deduced from these studies provide useful insight into the corrosion of glass.

5.3 Surface Layers in Leached Borosilicate Glass High-Level Defense Nuclear Waste Forms

This section of the report discussed the physical and chemical properties of the surface layer that forms on a borosilicate glass upon leaching. Based on their analysis, the following general picture emerges (Figure 5.1). At the glass-solution interface, crystalline precipitates form among a layer of amorphous precipitates. Adjacent to this layer and beneath it is a porous hydrated region labeled the altered layer in the figure. This altered layer may be composed of several thin layers of precipitates of varying compositions. Below the altered layer is a thin (< 1μm) reaction zone which exhibits depletion of soluble species (B, Li, and Na). The breakdown of the glass network structure and release of elements occurs in this reaction zone. Although it is not clear from the text, this reaction zone is apparently the protective layer discussed in the preceding section.

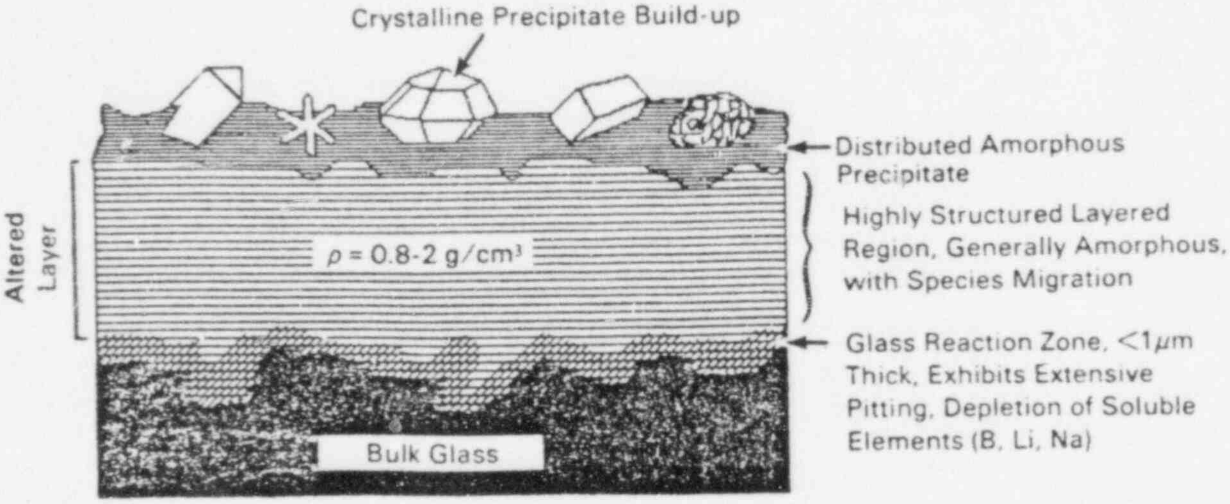

Figure 5.1 Physical characteristics of a borosilicate glass upon leaching

The exact nature of the surface depends on flow rate and groundwater composition. Low flow and more concentrated leachants (silicate water) produce thinner, higher density layers than high flow leachants. The presence of metallic iron in oxic leachants allows the formation of iron silicates which prevents silica saturation in solution and leads to thicker layers dominated by iron chemistry.

Based on the surface analysis techniques, the following leaching mechanisms have been determined:

a) Rapid release of soluble species such as B, Li, and Na.

b) Early precipitation of insoluble species such as Mg and Ca.

c) Iron and silicon in solution form colloids which can absorb charged particles (e.g., actinides and rare earths). These complexes can agglomerate and produce flocculent amorphous precipitates.

d) Saturation with respect to iron, silica, and aluminum occurs and hydrated precipitates form in the altered layer.

This study determined the disposition of elements in DWRG upon leaching, as listed in Table 5.1. However, it was stressed that even after one year of leaching, the system has not reached equilibrium and other crystalline phases may form in time. Thus, prediction of long-term saturation concentrations based on thermodynamic data is complicated by the formation of metastable phases.

Table 5.1 Disposition of elements in DRWG upon reaction with water. (PNL-5157)

Al	analcime and altered layer of glass
B	primarily solution, also in analcime (partial replacement for Al) and in Li-B-Si
Ca	various crystalline calcium silicate phases
Cs	analcime (partial replacement for Na)
Fe	altered layer of glass
Li	primarily solution, also Li-B-Si crystalline phases
Mg	smectite
Mn	primarily altered layer of glass, also one of the crystalline calcium silicate phases
Na	solution, analcime and weeksite
Ni	altered layer of glass
Si	the crystalline phases, the altered layer of glass and solution
Sr	partial replacement for Ca in one of the crystalline calcium silicate phases
U	weeksite
Zr	altered layer of glass

5.4 Environmental Interactions

The leachate which eventually contacts the waste glass will have passed through the repository rock, backfill (if present), a corroded metal overpack and canister in the presence of a radiation field. All of these will influence the groundwater chemistry. This section of the report presents experimental results on the influence of these parameters (except radiation, which is covered in another segment of the report) on leaching.

Experiments were conducted in the laboratory and in situ at the granite mine in Stripa, Sweden. The laboratory results correlated well with the in situ tests. Both showed that leaching increases in the presence of bentonite or ductile iron. Bentonite provides sorption sites to remove species from solution and therefore drives the solution further from saturation, which increases the driving force for further glass dissolution. Iron promotes the formation of colloids that remove silica from solution.

The role of groundwater chemistry was investigated by conducting leach experiments in deionized, silicate, and brine waters. The silicate water represented a generic basalt site water and the brine solution represented a generic salt site water. In general, for most elements leaching decreased in the presence of repository-like groundwaters. However, for brine solutions the release into solution of Cs, Sr and Ca increases over that of deionized water. The reason for this is that formation of precipitates containing these elements in the altered layer is less likely in brine solutions. In general, the release of species from the altered layer is a strong function of water chemistry. When ductile iron is included in these leaching experiments, the beneficial effect of the groundwaters compared to deionized waters largely disappears, indicating that iron is controlling the leaching.

The presence of stainless steel, corroded stainless steel, Pb, Cu, and Ti caused little effect on the leach rate.

5.5 Dissolution of Specific Radionuclides

The release of long lived radionuclides received careful study because these nuclides will be most important in determining the long term safety of waste disposal. The nuclides studied included Tc, U, Np, and Pu. All of these are multivalent, and therefore the Eh was measured and controlled in the experiments.

Tc and U release were strongly influenced by Eh, showing increasing solubility with increasing Eh. Release of Tc was decreased by several orders of magnitude under highly reducing conditions. The role of Eh on Np and Pu was not investigated, although similar trends are expected.

Under oxidizing conditions, release of Tc follows linear to parabolic kinetics. This was interpreted to be due to the formation of a protective layer on the glass in which Tc release was limited by diffusion through this layer. However, none of the other elements of the glass, including the actinides, exhibit this kinetic behavior and it is not clear that the interpretation is correct.

Uranium dissolved incongruently under oxidizing conditions. However, it dissolved with the same kinetic behavior as the glass forming elements. The departure from congruent dissolution changed with pH. At low pH, <3, normalized uranium release was greater than B release, while at high pH, >9, it was significantly lower than B release.

Actinide release from DWRG doped with Pu or Np was studied in deionized, brine, simulated basalt, and tuff J-13 waters under oxic conditions. Release of Pu or Np was controlled by the alteration of the glass network. Therefore, leachants containing silica had lower releases of Pu and Np. The addition of ductile iron increased the release of Pu and Np, and the increase is smaller in brine as compared to other solutions. However, most of the Pu and Np released form colloids with the iron, and the actual solution concentration decreases. In general, U had a much lower tendency to form colloids than Np or Pu, and therefore should not be used as an analogue for these nuclides.

Three cautionary statements were given against the use of available solubility limits for predicting solubility controlled release. First, the actinide bearing solids that form upon glass dissolution are "chemically complex, hydrated, amorphous compounds rather than the simple oxide or hydroxide compounds used in solubility studies." Second, steady-state concentrations observed in glass/ground water tests are determined by a dynamic balance between precipitation and dissolution of different solids and are not true thermodynamic solubilities. Third, the solubilities obtained up to this time have been determined under conditions that differ greatly from expected repository conditions.

5.6 Radiation Effects

Radiation can influence glass leaching in three ways: radiation damage to the glass waste form, radiation damage to the host rock, and radiolysis of the groundwater. Radiolysis is expected to be the major effect. Radiolysis can produce more chemically aggressive species in the groundwater, and thereby increase leaching. Also, α-radiolysis can raise the Eh of the leachant which raises the saturation concentration of multivalent nuclides.

The influence of γ-radiolysis on waste form leaching was investigated with the result that the leach rate increased by as much as a factor of 7 in short term tests with dose rates greater than 10^5 R/hr. At doses less than 10^5 R/hr there was a marked decrease on the effects of γ-radiolysis. Another interesting effect was that at a temperature of 90°C, radiolysis had little effect on leaching; whereas at 50°C, radiolysis increased the leach rate by a factor of 3. This was attributed to other leach rate mechanisms dominating the radiolysis effects at higher temperature.

α-radiolysis was studied by doping DWRG with Pu-238 and leaching in deionized water at 40°C. This increased the leach rate by a factor of 2 over the leach rate of DWRG doped with Pu-239, which has a much longer half-life and therefore a lower α-dose rate.

Radiation damage to salt rock can cause colloid formation. Models of this process predict that under repository conditions as much as 25% of the NaCl near the waste canister can be converted to Na colloids. However, the model ignores the effect of dose rate which has been experimentally shown to be important, and it does not model any saturation of damage which typically occurs in radiation-damaged solids. Thus, the accuracy of this model is questionable and further work is necessary before accepting the model's predictions.

When groundwater contacts radiation-damaged salt, sodium hydroxide will form. Provided the chlorine gas induced by radiation escapes before water arrives, the presence of sodium will cause an increase in pH. If the chlorine remains in the rock salt, a strong acid (HCl) and a weak acid (HOCl) will form and the pH will be controlled by the weak acid. Thus, the major issue that needs to be addressed involves the release of chlorine gas from irradiated salts. Currently this question has not been experimentally resolved. However, an attempt to measure chlorine release is being performed by Levy and coworkers at BNL in a DOE-sponsored effort.

Computer modeling of the species produced by radiolysis has had some success on simple systems. However, the scarcity of reliable reaction rate constants and uncertainties in the amount of species produced per deposited radiation energy (G-values) hamper the use of these codes for the more complicated repository environments.

In general, the influence of radiation on leaching is not well known. Very little work has been done on radiolysis as a function of temperature (most studies were carried out at 25-90°C), groundwater chemistry (especially silicate waters), and dose rate. Successful long term prediction of radiolysis effects will require a better data base geared towards the complex repository environment.

5.7 Phenomenological Models of Nuclear Waste Glass Leaching

Long term prediction of waste form leaching will require development of mathematical models that predict leaching behavior. There are three types of mechanistic modeling. The first views processes in the waste form (such as diffusion) as the rate controlling process. The second approach takes a reaction kinetic viewpoint and assumes leaching is controlled by chemical reactions between the solution and glass. The extreme in this approach is to assume that thermodynamic considerations control glass dissolution. The third type of model uses an interactive approach between the glass and solution.

Each of these approaches has had some success for simple glass-groundwater systems. However, all of the models are simplifications of a complex problem, and none of them can predict glass dissolution under all conditions. Kinetic approaches are limited by the large number of possible reactions and the lack of data on the reaction rates. Thermodynamic approaches are limited by the lack of data and long time required to reach equilibrium for the chemically complex precipitates that form on the glass surface.

To overcome the problems inherent in mechanistic approaches, this study developed a phenomenological approach in which physical phenomena are included in mathematical response functions that are constructed to reproduce experimental data. This approach guarantees that the response has the proper limiting behavior and has been successful in reproducing trends in experimental data. However, it will be difficult to justify use of this type of model to predict long term behavior because it is essentially an empirical fit to the data, and if the rate limiting conditions change (such as a change in solubility limit due to formation of alteration products) as the leaching process evolves, the model will not be able to predict this.

5.8 PROTOCOL, A Numerical Simulator for Glass Dissolution

PROTOCOL, a program to correlate leaching data, has been developed as part of the Leaching Mechanisms Program. The code has been constructed in a general manner, allowing flexibility in use and the ability to handle modifications in correlations as better models become available. The code has the capability to describe glass dissolution based on either kinetic or thermodynamic considerations. The computations proceed through real time increments as opposed to reaction path increments found in many geochemical codes. Finally, the code has the capability of estimating the standard Gibbs free energy function of poorly characterized solid phases. This may be useful in attempting to identify the crystalline phases that form on the glass surface.

To demonstrate the capabilities of the code, PROTOCOL has been used to model the dissolution of silica as a function of temperature, flow rate, surface area to volume ratio, and initial silica content of the water. The stability of various elements, as measured by free energy, contained in SRL-131 and DWRG glass as a function of pH and surface area-to-volume ratio was also studied. Based on these studies, it was concluded that the glass/solution interface exhibits a metastable equilibrium which can be modeled through a thermodynamic approach. Although the results of these computer studies reproduced experimental trends, they were not compared to experimental data.

PROTOCOL is in the developmental stage and requires further work before it will be complete. Areas identified for improvement include the improvement of the thermochemical data base, better models for activity coefficients, better numerical techniques to insure the chemistry segment of the code converges to the proper solution, and addition of the capability to monitor changes in solution pH as the glass dissolves.

The data base needs to be improved in three areas: a) most of the data exist only for complexes at 25°C; at other temperatures extrapolation procedures are used; b) there is little data on the precipitates that form in the altered layer, and c) better data and computational approaches are needed for redox reactions; currently all redox reactions are equilibrated to a user-defined Eh. The models for activity coefficients need to be improved to allow modeling of concentrated ionic solutions such as brines.

Appendix B of the report describes the input required for use of PROTOCOL.

5.9 Leaching Mechanisms in Polyphase Ceramic High-Level Nuclear Waste Forms

Initially, the Leaching Mechanisms Program was also designed to study leaching of crystalline ceramic waste forms. However, one year into the program, a decision to use glass as the waste form for defense wastes was made, and the study of leaching of crystalline waste forms was discontinued. The results of the work done on crystalline ceramics, presented in Appendix C of the report, are that polyphase ceramic leaching was phase-specific with the dissolution kinetics and activation energies of individual phases being comparable to the pure phase counterpart. Second, there was no formation of a hydrated gel layer on the surface of crystalline ceramics. However, for the cermaic phases which readily dissolve, alteration products form on the surface indicating solubility constraints are important in the long term. For the chemically more durable phases, the kinetics of dissolution controlled release.

The two best ceramics developed during the study were SYNROC-D and an alumina-silica based ceramic called CSRL-60. SYNROC-D contained hercynite-type spinel, ulvo-type spinel, nepheline, zirconolite, and perovskite phases. The actinides associate with the zirconolite and perovskite phases, which were more durable than the nepheline phase that contains most of the alkalis. CSRL-60 was composed of magnetoplumbite, nepheline, spinel, corundum, and uraninite phases. In this ceramic, the actinides would enter the uraninite phase and the rare earths and strontium would enter the magnetoplumbite phase. Again, these phases are more durable than the alkali-containing nepheline phase.

5.10 Summary and Conclusions

The report provides a comprehensive description of all the leaching work performed on SRL-131 and DWRG glasses and a general review of most of the leaching work performed on other nuclear waste glass. For this reason, it is an extremely useful document.

The information generated by this study, however, is presented in a somewhat disjointed manner. There was no real attempt made to integrate the knowledge gained into a complete picture of leaching under repository relevant conditions. The summary and conclusion section located at the beginning of the report simply reproduces the summary section of each of the seven chapters. Consistent with this, there are no recommendations for future work that would be required to supplement this study and help demonstrate acceptability of glass as a waste form.

The report, as written, makes a conscious effort to avoid drawing conclusions on whether the glass is an acceptable waste form or whether it is capable of meeting regulatory criteria on controlled release. The report concentrates on a presentation of the modeling and data obtained by the investigations performed in this program. This contrasts with the presentation of this work at the DOE Leaching Mechanisms Workshop held in September 1984, (Sullivan, T., and E. Gause, 1984). At this meeting it was stated that DWRG could meet the controlled release requirements, provided the temperature was kept below 90°C and the flow rate and groundwater chemistry do not change drastically from anticipated conditions.

Furthermore, the abstract of this report found in the National Technical Information System (NTIS) clearly draws conclusions as to the relevancy of this work to repository situations. This abstract states: "The participants reached a consensus that solubility of the leached glass species, particularly solubility in the altered surface layer, is the dominant factor controlling the leaching behavior of defense waste glass in a system in which the flow is constrained, as it will be in a deep geologic repository. Also, once the surface of waste glass is contacted by water, the kinetics of establishing solubility control are relatively rapid. The concentration of leached species reach saturation or steady state concentrations within a few months to a year at 70 to 90°C. Thus, reaction kinetics, which were the main subject of earlier leaching mechanism studies, are now shown to assume much less importance. The dominance of solubility means that the leach rate is, in fact, directly proportional to groundwater flow rate. Doubling the flow rate doubles the effective leach rate. This relationship is expected to obtain in most if not all repository situations." The reason for the discrepancy in conclusions between the abstract and report is unknown.

Also, the comment on reaching steady state concentrations after a few months to a year is not necessarily justified by the data. Static leaching of SRL-131 glass doped with actinides at 90°C in deionized water show a continual rise in U and Np solution concentration throughout the duration of a 546-day test (Bates, J.K., and others, 1983). This report (Bates, J.K., and others, 1983) suggests that longer leach tests containing a complete representation of all the minor elements expected in the waste form are necessary to determine the composition of the leached layers and alteration products that will form in an actual waste glass. Also, in the first chapter of the report an estimation of the time required for the appearance of visible crystals on the surface of DWRG was given as approximately 4 years at 90°C and 20 years at 70°C.

Even though this report does not specifically attempt to draw conclusions as to the acceptability of glass as a waste form, it is a source of a tremendous amount of information which may be useful in modeling glass leaching and demonstrating with reasonable assurance that glass waste forms comply with regulatory criteria. With this in mind, the following comments on the status of glass leaching and the work performed for this report are appropriate:

- Currently, there has been no leaching experiment that simulates the likely repository environment. This includes leaching of aged glass which is altered due to radiation damage and hydration through contact with a humid environment.

- This study emphasized leaching of SRL-131 and DWRG glasses, neither of which is likely to be the composition chosen for final burial. Furthermore, these glasses did not contain defense waste. This may be of extreme importance because slight changes in SRL-131 glass composition have been shown to drastically change the composition of the leached layer and alteration products (Bates, J.K., and others, 1983). This effect is most notable for actinide and rare earth elements which are the most important to understand for long term safety assessments.

- A majority of these tests were conducted in deionized water, which is not directly applicable to predicting repository leaching performance. With the exception of Stripa groundwater, the groundwaters used in the leaching experiments simulated natural groundwaters and differ slightly from expected repository waters.

- Leaching tests were conducted at a maximum temperature of 90°C, the maximum temperature expected in a salt repository for defense high level waste. However, the maximum expected temperature in a basalt repository is 150°C, and 95°C in a tuff repository. Also, a recommendation has recently been given to bury defense wastes in civilian repositories. If the defense wastes are co-mingled with hotter civilian wastes, the temperature may exceed those previously stated.

- With the exception of the tests at the Stripa mine, there was no attempt to measure the uncertainty of applying laboratory data to an actual repository system.

- Colloid formation was shown to increase release from the glass. However, the mechanism of colloid formation, the species associated with and the amount of colloids likely to be formed, and colloid transport away from the waste form were not addressed, and little information exists to resolve these issues.

- Current understanding of leaching mechanisms does not permit an accurate, unquestionable long term prediction of leach rates for all species. To obtain an accurate prediction would require a better, more quantitative understanding of precipitation phenomena in the altered layer, colloid formation and transport, the interpretation and influence of Eh on leaching, the influence of groundwater chemistry on leaching, and radiation effects in groundwaters. Even obtaining conservative upper bounds is a difficult task.

5.11 Reference

Bates, J. K., D. J. Lam, and M. J. Steindler, "Extended Leach Studies of Actinide-Doped SRL-131 Glass," published in Scientific Basis for Nuclear Waste Management, Vol. 15, 1983, pp. 183-190.

PNL-5157, "Final Report on the Defense High Level Waste Leaching Mechanism Program," J.E. Mendel and others, Pacific Northwest Laboratory, 1984.

Sullivan, T. and E. P. Gause, "Trip Report on the US-DOE Leaching Mechanisms Workshop Held in Germantown, Maryland, September 18-19, 1984," Brookhaven National Laboratory, NWM-MF-13, October 1984.

6. REVIEW OF SELECTED PAPERS PRESENTED AT THE "WASTE MANAGEMENT '85 CONFERENCE."

BNL staff attended the Waste Management '85 Conference held in Tucson, Arizona, on March 24-28, 1985. The meeting had technical sessions on both high and low level waste isolation in the United States. On the first morning, the meeting began with a session on regulatory perspectives and progress in siting HLW repositories. In the afternoon, the program presented discussions on interactions between various Federal and State agencies involved in the waste management problem. These sessions described the managerial aspects of waste management and set the background for the technical aspects presented in the last three days of the conference.

A number of papers pertaining to disposal of HWL in the areas of spent fuel leaching, glass leaching, modeling waste package performance, canister corrosion, and interactions between the DOE and NRC were presented. With the exception of presentations made by the NRC staff, reviews of the most relevant presentations are given below.

DOE Perspective on the Regulatory Structure (R. Stein, DOE)

Ralph Stein's presentation dealt with the interplay between DOE and the regulatory agencies involved in high-level waste management (NRC and EPA). He cited the fact that the Nuclear Waste Policy Act of 1982 calls for discussion between DOE and NRC during the pre-licensing period to identify and resolve issues. It was admitted that NRC was faster to recognize the need for this, but DOE now clearly sees the benefits of early interaction with the regulatory agencies. Stein felt that the NRC is currently giving good guidance to DOE with regard to regulatory issues.

One significant problem that DOE has experienced concerns the definition of "reasonable assurance" with respect to engineered system performance. From Stein's point of view it is connected with the question "How much data and analysis is sufficient to verify performance." DOE intends to address this difficulty in forthcoming Site Characterization Plans which will identify technical issues together with a description of the type of work which DOE will undertake in order to resolve them. Public hearings will also be held in order to determine "How much data is enough."

In order to address NRC concerns on quality assurance in DOE programs, Stein stated that DOE now had a broad scoping document defining the quality assurance program. More detailed and specific quality assurance plans have been prepared within the Office of Geologic Repositories. There is also in place a program for internal quality assurance training and the review of quality assurance. Part of the DOE quality assurance program was developed from knowledge obtained from NRC presentations in this area. DOE intends to cooperate with NRC in the establishment of a "safety classification system" which will identify critical issues requiring extra quality assurance.

In regard to underground testing work at proposed repository sites, NRC believes that most testing should be completed prior to construction authorization. However, DOE feels that much work will continue after authorization in order to establish a more comprehensive data base.

The National HLW Management Systems (W. Purcell, DOE)

Bill Purcell's talk discussed many of the major issues involved in managing the HLW system. The talk began with the statement that the DOE is committed to receive spent fuel by 1998. Although it was acknowledged that slippage in the current work schedules has occurred, he felt that the delays were necessary to insure safety. The major emphasis of the talk centered around Monitored Retrievable Storage (MRS) systems. The MRS would receive spent fuel, consolidate and package the fuel for burial and store it on a temporary basis. The advantages of an MRS are:

- It could receive spent fuel earlier than a repository.
- It would be a dedicated facility, thus allowing increased efficiency, better quality control, and it would be easier to manage.
- It would allow dedicated shipments to the repository, thereby optimizing the load and number of shipments.
- It would provide increased storage for spent fuel.

As currently planned, the MRS facility would be located in the east as close as possible to the center of the spent fuel inventories. It was emphasized that the MRS is not a repository substitute. However, DOE has concluded that the MRS would be beneficial and will integrate it into the Mission Plan for the entire disposal project and has set a June 1, 1985, deadline for submitting the proposal to Congress.

Other points of interest in this presentation were that currently, the DOE believes, it is not necessary to adjust the 1 mil/kWh charge for waste disposal assessed on HLW generators. Also, in the near future, DOE will recommend to Congress that defense waste be disposed of in a commercial repository because of economic considerations. The government will pay its portion of the disposal costs.

Radionuclide Release From PWR Fuels in a Reference Tuff Repository Groundwater (C.N. Wilson and V.M. Oversby, Westinghouse Hanford and LLNL)

Charles Wilson presented a paper on the solubility of radionuclides from PWR spent fuels in J-13 ground water obtained from the Yucca Mountains site in Nevada. In the investigation, which is part of the Nevada Nuclear Waste Storage Investigation Project (NNWSI) Spent Fuel Leaching/Dissolution Test Program, radionuclide release is measured from spent fuel specimens representing a range of possible fuel degradation states thought to be possible during the post containment period. Four test specimens were used:

- Slit defect on the cladding,
- Hole defects, two laser-drilled holes in the cladding,
- Undefected rod sections.

The tests were run in air at ambient hot cell temperature.

A test vessel containing the specimen was initially filled with 250 ml of J-13 water. Solution samples of 10-25 mL were periodically removed and replaced with fresh J-13 water. At the end of a test run, the final solution, the specimens, and water used to rinse deposits off the apparatus were all analysed. These test results are compared with earlier tests carried out in deionized water.

Uranium, Pu-239 + Pu-240 and Cs-137 contents in unfiltered solution samples are plotted in Figures 6.1 to 6.3 for the various tests.

Uranium concentrations in the J-13/Turkey Point (TP) bare fuel test remained nearly constant at 4 to 5 μg/mL. In the DIW/H.B. Robinson (HBR) bare fuel test, it decreased to 1.2 μg/mL from a maximum of 4.5 μg/mL. In the DIW/TP bare fuel test, the U content fluctuated to a greater extent. A 202-day solution sample had showed the presence of colloids or fine undissolved particles of uranium. When the test was continued to 250 days, it appeared that much of this colloidal phase may have precipitated. Am-241 and Cm-244 also behaved similarly.

Plutonium solution activites in the DIW/TP μg/mL tests were in general about an order magnitude higher than those measured in the J-13 water tests.

Due to the high activity and solubility of Cs-137 in the fuel-cladding gap, Cs-137 solution activity provides a means to monitor test performance. The relatively fast buildup of Cs-137 solution activity in the slit defect and hole defects tests to levels approximately equal to that in the bare fuel tests indicated that the water entered and filled the fuel/cladding gap. The fact that no increase occurred in Cs-137 solution activity provides a means to monitor test performance. The relatively fast buildup of Cs-137 solution activity in the undefected specimen tests indicated that these fuel specimens did not leach.

Fractional release of each radionuclide was calculated by dividing the total measured release by 10^{-5} of the radionuclide inventory, and the results are shown in Table 6.1 Even though, the total release for each of the radionuclide was calculated for the duration of the test (223 days), in all the bare fuel tests, the total release was more than the NRC limit of 10^{-5} of the inventory per year.

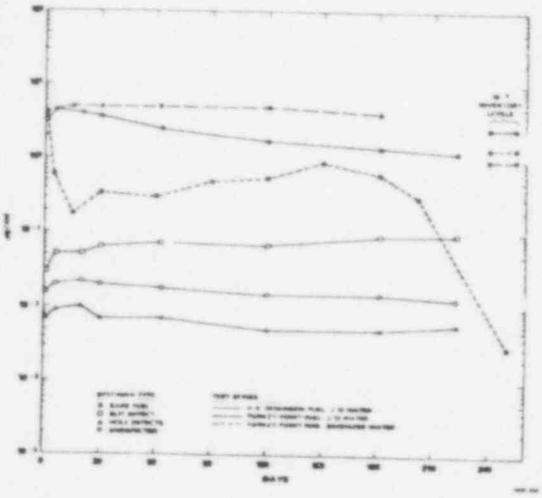

Figure 6.1 Uranium in unfiltered solution.

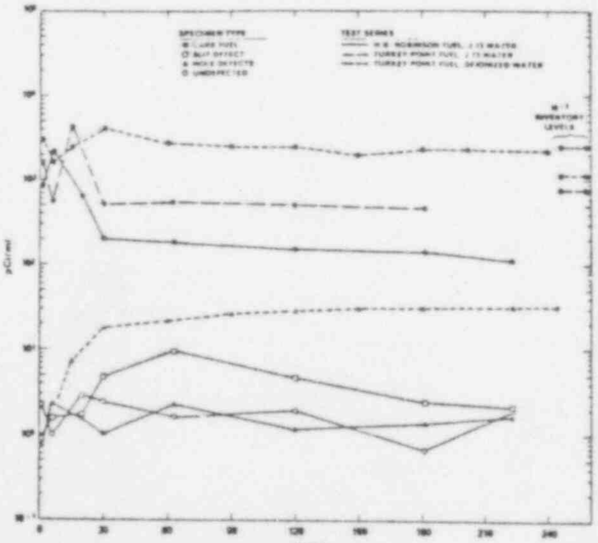

Figure 6.2 $^{239} + ^{240}Pu$ activity in unfiltered solution.

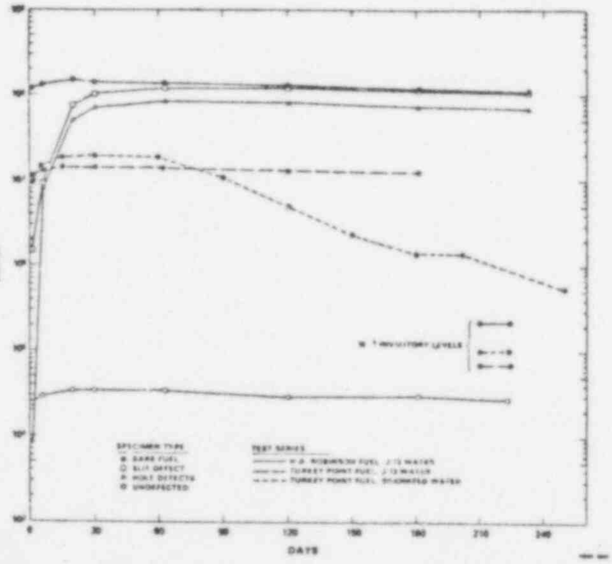

Figure 6.3 ^{137}Cs activity in unfiltered solution.

Table 6.1 Total measured release divided by 10^{-5} inventory.

	SERIES	BARE FUEL	SLIT DEFECT	HOLE DEFECTS	UNDEFECTED
Uranium	J-13/HBR	5.42	0.044	≈0.005	<0.008
	DIW/TP	21.2	0.065	0.032	0.010
Pu-239+	J-13/HBR	7.04	0.008	≈0.002	≈0.002
Pu-240	DIW/TP	22.4	0.20	0.042	0.021
Am-241	J-13/HBR	7.76	0.008	≈0.002	≈0.003
	DIW/TP	17.2	0.152	0.019	0.008
Cm-244	J-13/HBR	6.54	0.007	0.001	≈0.002
	DIW/TP	21.5	0.35	0.026	0.006
Np-237	J-13/HBR	≈6.4	--	--	--
	DIW/TP	≈18	≈0.2	--	--
Cs-137	J-13/HBR	683	567	362	≈0.7
	DIW/TP	≈230	110	50	0.04
Tc-99	H-13/HBR	20.2	2.46	≈1	--
	DIW/TP	152	81	--	--

The conclusions from the above table are:

1. Greater release occured in the DIW/TP tests relative to the J-13 HBR tests;

2. Actinides appear to be released congruently; and

3. Cs-137 and Tc-99 are released preferentially relative to the actinides.

Solution pH was measured in the various tests. A comparison of the change in pH is shown in Figure 6.4.

The J-13 water, containing about 120 μg/mL bicarbonate, became slightly basic during the tests, while the deionized water became slightly acidic. The pH of the later dropped to about 6 and remained around that value. Lower pH in the deionized water test may have resulted from radiolysis of dissolved air and water producing HNO_3. This HNO_3 radiolysis product would not have much effect on the J-13 water pH because of buffering by the bicarbonate.

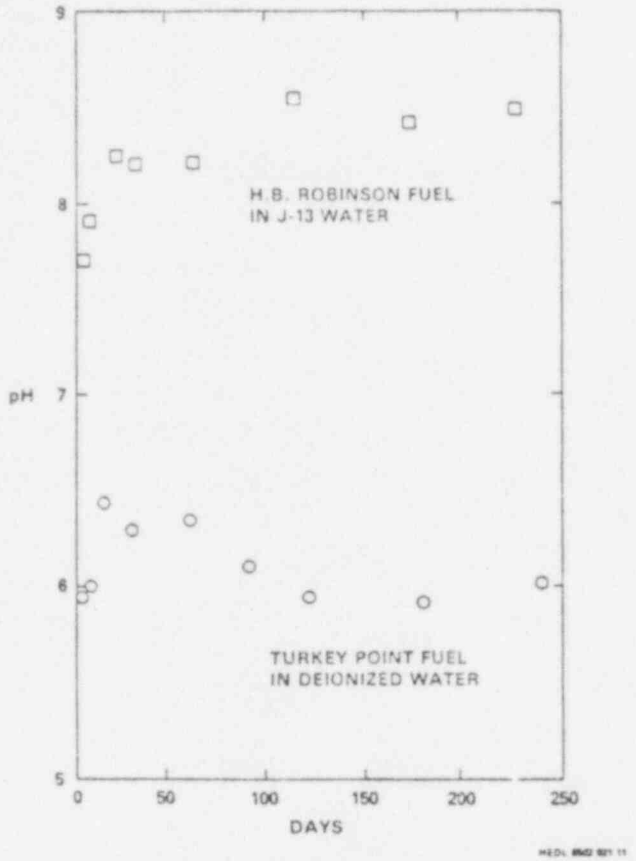

Figure 6.4 pH of solution samples taken from the H.B. Robinson fuel in J-13 water and Turkey Point fuel in deionized water - bare fuel tests.

The overall presentation, gives an understanding of the radionuclide solubilities in tuff groundwaters and deionized water. It also shows the effects of various defects on the spent fuel rods on the solubility and radionuclide release rate. However, there is some concern about the semi-static conditions used in the tests. A sample of up to 25 mL is about 10 percent of total solution in the test vessel. When several such samples are taken and replenished with fresh solution, that could give some error in the final analysis of the leaching rate. If indeed a 25 mL sample was necessary, the test should have been carried out with a higher volume of test solution. This replenishment rate does not correspond to the actual replenishment conditions for a tuff repository, which is <1 mm/year.

Used Fuel Dissolution Studies in Canada (L.H. Johnson, N.C. Garisto and S. Stroes - Goscoyne, Whiteshell Nuclear Research Establishment, AECL)

Lawrence Johnson, of the Atomic Energy of Canada presented a paper on "Used-Fuel Dissolution Studies in Canada." This investigation was carried out to provide SYVAC (Systems Variability Analysis Code, developed by Canadian Nuclear Fuel Waste Management Program) with source-term models for the release of radionuclides from used fuel. The studies included leaching and dissolutions experiments on used CANDU fuel, as well as fundamental investigations of UO_2 electrochemical behavior for a range of solution chemistry conditions, in both the presence and absence of radiation fields.

The radionuclide release and migration through buffer material are represented in SYVAC by one-dimensional transport equations, which take into account diffusion, convection, sorption, radioactive decay and buildup. There are two source boundary conditions depending on the mechanism of release of radionuclides from the used fuel.

1. An instant release of a fraction of the inventory of some radionuclides upon container failure and contact of the fuel by groundwater. In this case, Cs-135 and I-129 from the fuel-sheath gap and UO_2 grain boundaries upon contact with groundwater.
2. A slow, solubility controlled, congruent release of radionuclides due to the dissolution of the fuel matrix itself. Here, it is uranium-solubility controlled dissolution of UO_2 grains. Validity of this model depends on the chemical stability of UO_2 and its exact dissolution mechanism under the geochemical conditions existing in the vault.

A qualitative picture of how the release of fission products such as Cs-137, Cs-135 and I-129 through a gap and grain boundaries may proceed is shown in Figure 6.5.

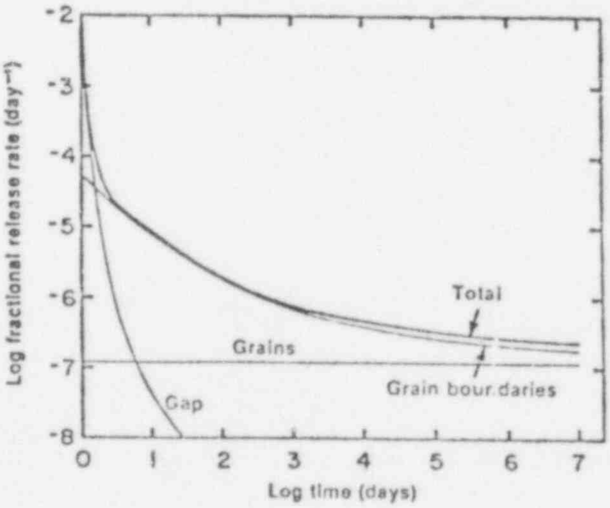

Figure 6.5 Fission-product release from UO_2 fuel in water, oxidizing conditions.

The gap and grain-boundary release curves shown above are only approximate, and may vary greatly depending on the fuel microstructure. The principal controlling factor in the release of radionuclides from used fuel is expected to be the rate of dissolution of UO_2, since more than 90% of the radionuclide inventory is contained within the UO_2 grains.

There are a number of uncertainties in the current understanding of spent fuel dissolution. In particular, because the difference in uranium solubility between reducing and oxidizing conditions is several orders of magnitude, one would expect this difference to be reflected in the dissolution rates. However, experimentally, little difference is found between the release rates of used fuel as a function of Eh. It has been speculated that this may be due to grain boundary leaching. Other uncertainties arise due to the influence of radiolysis and groundwater chemistry on leaching.

To further understand the radionuclide release under different geochemical conditions, experiments are being conducted under reducing conditions and various groundwater compositions, including the effects of α-radiolysis. These studies will provide data on radionuclide release under the expected vault conditions and will lead to the development of methods to mitigate the effects of radiolysis by controlling the near-field redox conditions.

Solubility of Unirradiated Fuel in Granitic Groundwater (M. Nykyri and K. Ollila, Technical Research Center of Finland)

M. Nykyri of the Technical Research Center of Finland presented a paper on, "Solubility of Unirradiated Fuel in Granite Groundwaters." The dissolution experiments of unirradiated uranium oxide pellets in this work were carried out in oxygen-free containers and a glove box, and in an anaerobic autoclave system. Two different synthetic groundwaters corresponding to undisturbed groundwaters deep in the granite bedrock, and another with high carbonate content, were employed in these tests. The high carbonate groundwater takes into account the effects of bentonite present around the spent fuel canisters in the repository. Also two natural groundwaters were used. Other experimental conditions were:

pH	4.5 to 11
Eh	0.1 to -0.4 V
Temperature	25°C and 60°C

The compositions of the groundwater used in the experiments are shown in Table 6.2

The tests were carried at a pressure of 10 MPa. The pH is adjusted by varying the composition of $HCO_3^- - CO_3^{-2} - OH^- - H^+$. The Eh was controlled by Fe(II) content.

The dissolution rates of uranium in the various leaching solutions are shown in Table 6.3 The dissolution rate varied from $2x10^{-8}$ to $2x10^{-7}$ g cm^{-2} d^{-1} at pH 8 to 9. From the table, it is seen that there is a wider range for the solubility values in the literature, i.e. 10^{-9} to 10^{-6}

Table 6.2 Groundwater compositions.

Component	Dimension	Olkiluoto groundwater (Sample YD2, 70m, 30.8.1982) (natural)	Stripa groundwater (Sample M3/82-09/1) (natural)	Undisturbed granite ground-water[1] (synthetic I)	Groundwater in the presence of bentonite clay[8] (synthetic II)
pH	1	8.2	8.3	8...9	8...9
Eh	V	-	-	-0.1	-0.4...0
Alkalinity	mval/l	5.9	1.4	-	-
Electric conductivity	mS/m	8.7	28	-	-
Permanganate number $KMnO_4$	mg/l	50	4	-	-
Phosphate PO_4^{3-}	mg/l	.011	< 0.1	-	0.01
HPO_4^{2-}	"	-	-	-	0.4
Sulphate SO_4^{2-}	"	180	6.0	9.6	50
Chloride Cl^-	"	20	37	70	80
Fluoride F^-	"	0.47	5.3	-	7.5
Bicarbonate HCO_3^-	"	360	86	120	400...600
Nitrite NO_2^-	"	< 0.1	< 0.001	-	-
Nitrate NO_3^-	"	< 0.1	< 0.02	-	-
Iron Fe_{tot}	"	0.04	< 0.02	(2...3)	< 5
Silica SiO_2	"	13 (Si)	< 1	12	20
Potassium K^+	"	17	0.26	3.9	5
Sodium Na^+	"	77	50	65	300...500
Ammonium NH_4^+	"	< 0.01	< 0.01	-	-
Calcium Ca^{2+}	"	69	14	18	20
Magnesium Mg^{2+}	"	39	0.25	4.3	5
Manganese Mn^{2+}	"	1.3	< 0.02	-	-

Table 6.3 Dissolution rates of uranium.

Water	Oxygen content (mg/l)	Temp. (°C)	Dissolution rate ($g\ cm^{-2}\ d^{-1}$)	Time
Deionized	8...9 Air-saturated	25	$5 \cdot 10^{-8}$	After 732 d
Olkiluoto groundwater	< 0.01 Oxygen-free	25	$1 \cdot 10^{-7}$	After 612 d
Stripa groundwater	"	25	$2 \cdot 10^{-7}$	"
Olkiluoto groundwater	2...3 Mildly oxidizing	60	$2 \cdot 10^{-8}$	"
Stripa groundwater	"	60	$2 \cdot 10^{-7}$	"
Literature[6]	-	-	$10^{-9}...10^{-6}$	-

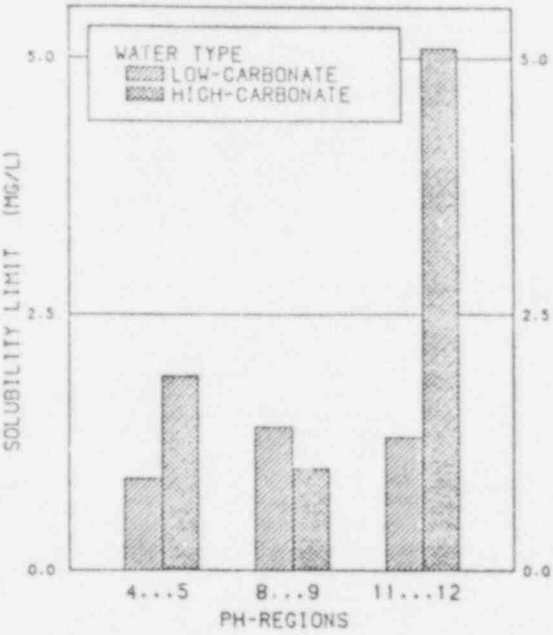

Figure 6.6 Solubility limit of uranium as a function of pH. The low-carbonate water refers to Synthetic Groundwater I and the high-carbonate water to Synthetic Groundwater II.

The Eh has great influence on the solubility rate; less solubility for lower Eh. Even with higher carbonate content, the solubility stays low if a low Eh is maintained.

Figure 6.6 shows the effect of pH on uranium solubility in synthetic groundwaters. From preliminary tests, it is seen that for higher carbonate content groundwaters, the solubility increases as pH increases. However, at pH 8-9, the solubility value is lower than at pH 4-5. This needs to be confirmed. If indeed, the solubility decreases, it is possible that some other mechanism may be involved such as precipitation of uranium from the solution.

The investigations confirm that the solubility of uranium in granite groundwater varies strongly with the groundwater conditions. As a preliminary investigation, the results are useful in developing the test method and to check the effect of pH, Eh and chemical composition of the groundwater on the solubility of uranium.

A Generalized Waste Package Containment Model (A. Liebetrau, Pacific Northwest Laboratory)

As part of the development of a unified and comprehensive geologic repository performance model, PNL is developing a generalized waste package system containment model. This model is currently at the conceptual stage and consists of a series of modules which represent the physical processes leading to the degradation of the barriers and penetration of groundwater to the waste form. Through proper choice of the modules any of the three repository sites could be represented. Output from the containment model will be a probablity density function for the time of penetration. Canister and Zircaloy cladding corrosion and aperture growth will be modeled. The corrosion model will consider fracture, uniform corrosion, stress-corrosion, and pitting. One goal of this modeling approach is to obtain "realistic" estimates not just bounding estimates of the penetration time. However, to do so requires additional complexity in the models and requires use of models that can not be supported by currently available data. This is particularly true in modeling corrosion in a repository environment with a radiation field present where even general corrosion mechanisms are not well characterized. Repository relevant data for this corrosion phenomena such as pitting or aperture growth are sparse and may not support "realistic" predictions. However, the modular approach used in this model will allow easy adaptation of improved models and data if they become available. In general, this modeling approach is a step in the right direction of realistic predictions of barrier degradation. However, unless these models are used to drive future experiments to obtain data required in the models, this approach will be hampered (by lack of data) in any attempt at obtaining defensible "realistic" predictions of barrier degradation.

Model Reliability and Software Quality Assurance in Simulation of Nuclear Fuel Waste Management Systems (M. Elas, Dutch Agricultural University, T. Oren and G. Sheng, University of Ottawa)

Morris Elas discussed computer model reliability in general terms by dividing it into two components; code performance and quality of models.

Measures of performance include:

- Correctness as a program and a mathematical procedure. This includes validation of the code;
- Flexibility of the program to handle a wide range of problems;
- Sensitivity of the program to insure that numerical errors are bounded;
- The number and types of alarms and traps that are activated when the computed solution does not make physical sense, or leaves the range of model applicability.

The quality of the model can be judged in two segments. The model realism, that is its ability to reproduce experimental data. Demonstration of model realism involves verification of the code. The second criteria for model quality is the scope and fidelity of the code. This involves developing an understanding of the models and the data required to operate the models and then applying this understanding to determine the range of applicability of the models and availability of reliable data.

Grant Sheng discussed software quality assurance which he defined as a systematic program to assure that a computer simulation carries out its intended function. This QA program involves continual testing to find and correct the errors in the code, and documentation of the code and its evolution. Dr. Sheng stated that proper maintenance of codes is essential for QA and fitted many cases where extensive repairs are more expensive than development of the codes. Thus, careful code development is an important objective to minimize errors which will have to be corrected later.

These two presentations addressed software QA in nuclear waste management systems in only a cursory manner giving a few examples that would require better QA. However, the question and answer section following the presentations implied that the DOE believes software QA is an important control and they are focusing attention on this matter. In the future, all DOE computer codes will be subject to quality assurance programs.

Corrosion Performance of Metals and Alloys in Geochemical Environments

(R.A. Van Konynenburg and R.D. McCright, LLNL)

Rich Van Konynenburg briefly reviewed the container material corrosion program within the tuff repository development effort. Initially, the selection of candidate materials was based on four criteria: mechanical strength, fabricability/weldability, corrosion resistance and cost. Based on this selection analysis, Types 304L, 316L and 321 stainless steel, and Incoloy 825 were selected as candidate container materials. Most work to date has focused on these, but limited efforts have been spent on carbon steel (for use as a borehole liner) and copper based alloys.

The repository environment for spent fuel waste packages will consist of steam/air conditions for an initial period at least 100 y. For defense waste packages the repository would likely cool within about 200 y to 90°C at which point liquid water, rather than steam, would be present.

The maximum expected temperature of a container surface would be 270°C, and the water chemistry is assumed to be similar to J-13 well water having a pH of about 7 or slightly higher. The maximum gamma dose rate at the container surface was calculated to be about 10^5 R/h.

Most tests for corrosion have been in J-13 well water but in recognition of the likelihood of groundwater boiling effects some work has been conducted in J-13 water which was "boiled down" to give concentrated solutions.

To date, no stress-corrosion cracking has been observed for the stainless steels or Incoloy 825 in boiling J-13 water after 1 year of testing in the presence of a gamma field. Materials were in both the solution annealed and a sensitized condition (thermally aged for 24 h at 600°C). These materials also showed no signs of pitting or crevice attack after exposure to boiling J-13 water for times up to 10^4h (≈14 mo).

In the case of 1020 carbon steel, which may be used as a liner for the horizontal borehole concept, gamma irradiation increased the uniform corrosion rate by a factor of about two. This is generally consistent with other related work carried out in this country. No stress-corrosion cracking was noted.

Limited work carried out on copper showed that crevice corrosion occurs at room temperature in a moist air/gamma irradiation environment.

Work in the future for the LLNL program will involve even longer term test on the stainless steels to determine if stress-corrosion cracking can occur over very extended periods.

Characterization of SRP Glass (M.J. Plodinec, Du Pont)

John Plodinec described recent progress on the construction of the Defense Waste Processing Facility (DWPF) and in the characterization of the borosilicate waste glass it will produce. Currently, it is anticipated that cold testing at the DWPF will commence in 1988 and the following year actual radioactive waste will be processed.

Plodinec gave estimates for conditions expected in various host rocks for defense waste glass. They are as follows:

Parameter	Host Rock		
	Salt	Basalt	Tuff
Temperature Range (°C)	34-90	57-150	30-95
Pressure (psi)	2800	4700	Atmospheric

An interesting point to note is that for tuff the maximum anticipated temperature is at the boiling point of water at the repository horizon. Thus, liquid water will be present at repository closure and container corrosion will have to be considered at this early time. In earlier work carried out at LLNL it was shown that liquid water conditions would only occur after 100 years, leading to significantly lower rates of aqueous corrosion (McCright, R.D., and others, 1984).

An interesting correlation was described between the normalized weight loss for glasses (based on silicon) and the estimated free energy of hydration of the glasses. The mass losses were obtained from MCC-1 type tests and the free energies of hydration of the glasses were obtained by summation of the individual free energies of the glass components. It was found that the logarithm of the normalized mass loss is directly proportional to the free energy of hydration. This relationship is being used to predict glass durability as a function of glass composition and to explain surface alteration of glass during leaching.

Some multicomponent leaching tests were also described involving non-radioactive and radioactive glass leached in the presence of stainless steel (container material) and host rock. In the case of the radioactive glass, Cs, Sr, and Pu concentrations in the leachant approached equilibrium after about 40 days. A sample calculation based on the leaching data showed that the controlled release rates for these species lay in the range 1 part in 10^7 to 1 part in 10^8 per year.

Other items of interest reported by Plodinec were:

a) SRL is involved in several long term in situ testing programs at Stripa (Sweden), Mol (Belgium) and WIPP. In the Stripa work the tests have lasted for 2 years. It was found that glass alteration in the granite host rock occurs over an initial period of about 1 month, and, therefore, little change is noticed. In the WIPP program, SRL is supplying non-radioactive, full-sized glass monoliths contained in TiCode-12. These will be used to check container corrosion at temperature.

b) SRL has examined the effect of glass melter size on the durability of the glass produced. It appears that the larger glass melters produce a more durable glass.

Environmental Parameters Governing Release-Rates From High-Level Nuclear Waste Glass (P. Macedo, Catholic University)

Pete Macedo discussed the influence of flow rates and solubility limits on release from glass waste forms. His interpretation of leaching is that there are three regimes for release rate as a function of flow rate. At high flow rates release is limited by the dissolution kinetics of the waste form. At intermediate flow rates release is limited by solubility effects and is proportional to flow rate. At low flow rates release is limited by solubility and the rate of mass diffusion away from the waste form. Expected repository conditions fall under the low flow rate region.

Dr. Macedo postulated that upon leaching, formation of a crystalline alteration layer occurs which reduces and eventually prevents further leaching of the glass. The reason given for the reduction in leaching is that the alteration layer and the bulk glass reach equilibrium. This protective layer theory has been questioned and it has been argued that there is a continual but slow dissolution of the glass. Tests on PNL 76-68 glass indicate the alteration layer offers little protection against glass dissolution. Tests on SRL glass, the glass used in Catholic University experiments, indicate that the layer may be protective but are inconclusive. At this time, it is not possible to conclude that a protective alteration layer will form on a leached glass.

6.1 Reference

R.D. McCright and others, "Corrosion Test Plan to Guide Canister Material Selection and Design for a Tuff Repository," in Scientific Basis for Nuclear Waste Management VII, North Holland, 1984, pp. 309-318.

7.0 REVIEW OF RADIONUCLIDE INVENTORIES REPORTED IN THE SALT ENVIRONMENTAL ASSESSMENT (EA) REPORTS.

It is essential to accurately determine the mass inventory of the various nuclides in order to predict if the annual release rate of a specific nuclide from the waste form will exceed the NRC criteria of 1 part in 10^5 per year of the inventory at 1000 years. However, the inventories reported within each salt EA are not internally consistent and, therefore, the conclusions drawn regarding controlled release are open to question.

To illustrate the inconsistencies, Table 6-27 and 6-36 of the Richton Dome EA (shown here as Tables 7.1 and 7.2) will be examined. Table 7.1 presents several radionuclide inventories in 72,000 MTHM of spent fuel and civilian high level waste at 0, 200, and 1000 years after emplacement. Table 7.2 presents a comparison of spent fuel package release rates required to saturate incoming brine at 300 years with the NRC engineered barrier system release rate limits in NRC Rule 10 CFR 60. Part of this table is the nuclide inventory per package at 300 years. Tables similar to these can be found in each of the salt EA's.

Comparison of the inventories in these tables requires a conversion of the total repository inventory in curies from Table 7.1 to the number of grams per package. To accomplish this, the number of curies is divided by the specific activity (the number of curies per gram of material). This result is divided by the number of packages. For 72,000 MTHM with 4.6 MTHM per package there are 15,652 packages. It should be noted that Table 6-29 of the Richton Dome EA which gives repository storage parameters states that there will be 7899 packages. Presumably this design is for 36,000 MTHM in the repository. A detailed example of this calculation is provided in Appendix B and the results are presented in Table 7.3.

From Table 7.3 it is clear that the nuclide inventories from the two tables are often in strong disagreement. The element inventories at 300 years from Table 7.2 used in the release calculations are one or two orders of magnitude greater than the 200 year radionuclide inventories from Table 6-27 for C-14, Se-79, Sr-90 and I-129. Smaller but still substantial differences are found for cesium. Apparently the inventories in Table 7.2 account for stable or extremely long lived isotopes of these elements. If this is the case, the source and amount of these stable isotopes should be identified in the text. The actinide inventories show reasonable agreement within the two tables. However, it is interesting that there are 4.8 MTU in Table 7.2, yet the package design calls for 4.6 MTHM. Finally, the inventory of Sn-126 at 200 years from Table 7.1 is twice as large as the 300 year inventory from Table 6-35 of the EA report. Radioactive decay does not account for this discrepancy because the half-life of Sn-126 is 100,000 years.

Use of the undocumented inventories in Table 7.2 favors the probability of meeting the annual controlled release limit of 1 part in 10^5. In these calculations, release is assumed to be solubility limited and for elements with more than one isotope, each isotope is released in proportion to its isotopic fraction in the waste form. For example, if 0.029 gm/yr of carbon are

Table 7.1 Radionuclide inventories(a) in 72,000 MTHM of SFPWR and CHLW at various times after emplacement. (Tables 6-27 from Richton Dome EA).

Nuclide	Half-Life, yr	Inventory, Ci					
		0 yr		200 yr		1,000 yr	
		CHLW	SFPWR	CHLW	SFPWR	CHLW	SFPWR
C-14	5,730	89,500	89,500	87,300	87,300	79,300	79,300
Se-79	65,000	29,200	29,200	29,100	29,100	28,900	28,900
Sr-90	28.9	4.09E + 9(b)	4.09E + 9	3.50E + 7	3.50E + 7	0.202	0.202
Tc-99	213,000	933,000	934,000	932,000	933,000	930,000	931,000
Sn-126	100,000	55,300	55,300	55,200	55,300	54,900	55,000
I-129	1.60E + 7	2,250	2,250	2,250	2,250	2,250	2,250
Cs-135	2.30E + 6	24,200	24,200	24,200	24,200	24,200	24,200
Cs-137	30.2	5.87E + 9	5.87E + 9	5.77E + 7	5.78E + 7	0.542	0.542
Ra-226	1,600	0.026	0.026	0.858	8.65	4.69	226
Th-230	77,000	9.55	9.55	10.6	212	17.1	1,236
U-233	159,000	0.00976	1.96	22.7	27.9	152	232
U-234	244,000	430	86,100	745	132,000	964	145,000
U-238	4.47E + 9	114	22,900	114	22,900	114	22,900
Np-237	2.14E + 6	22,400	22,400	29,100	38,200	42,000	71,300
Pu-238	87.7	8.16E + 5	1.63E + 8	354,000	3.38E + 7	9,860	70,500
Pu-239	24,100	113,000	2.25E + 7	120,000	2.24E + 7	143,000	2.19E + 7
Pu-240	6,540	188,000	3.77E + 7	431,000	3.72E + 7	396,000	3.42E + 7
Pu-241	14.7	2.77E + 7	5.54E + 9	11,700	523,000	9,240	9,240
Pu-242	376,000	609	122,000	629	122,000	643	122,000
Am-241	432	1.21E + 8	1.21E + 8	8.83E + 7	2.26E + 8	2.45E + 7	6.27E + 7
Am-243	7,380	1.19E + 6	1.19E + 6	1.17E + 6	1.17E + 6	1.08E + 6	1.08E + 6
Cm-244	18.1	9.07E + 7	9.08E + 7	43,000	43,000	About 0	0.000003
Cm-245	8,500	10,000	10,000	9,850	9,850	9,220	9,230

Note: Apparent discrepancies may appear because of rounding to 3 significant figures.

(a) ORIGEN-2 computer runs made for SRPO data base - 32,717 MWD/tonne burnup with intermittent shutdowns.

(b) 4.09E + 9 = 4,090,000,000

Table 7.2 Richton Dome SFPWR package. Comparison of package release rates to saturate incoming brine at 300 years at the waste package boundary with NRC engineered system release rate limits in 10 CFR 60 (Table 6-36 from Richton Dome EA).

The final gross volume of incoming brine will be 0.14 m^3, made available by brine migration without a threshold thermal gradient.

The gross brine inflow rate is 7.3E-5 m^3 per year at 300 years after burial.

Element	Solubility,[(a)] grams/m^3	300 yr Package Inventory,[(b)] grams	Quantity Required to Saturate Incoming Brines, grams/yr	Nuclide	Activity From Package to Brine, Curies/yr	Ratio to 1000yr Nuclide Activity/ (1E-5 per yr)	Ratio to 1000yr Total Activity/ (1E-8 per yr)
Carbon	400.	831.	0.029	C-14	0.00021	3.8	2.5
Selenium	0.001	279.	7.3E-08	Se-79	5.3E-10	2.7E-05	(c)
Strontium	0.8	1,750.	5.9E-05	Sr-90	7.6E-06	58,000.	0.090
Technetium	0.001	3,813.	7.3E-08	Tc-99	1.2E-09	1.9E-06	(c)
Tin	0.0001	6,752.	7.3E-09	Sn-126	4.2E-12	1.1E-07	(c)
Iodine	600,000.	1,157.	44	I-129	0.0059	3,800.	71.
Cesium	600,000.	7,077.	44	Cs-135	0.010	620.	130.
				Cs-137	2.5	6.6E+09	30,000.
Radium	0.00042	0.0011	3.1E-08	Ra-226	3.1E-08	0.20	(c)
Thorium	0.001	1.2	7.3E-08	Th-230	1.3E-09	0.0015	(c)
Uranium	0.001	4,800,000.	7.3E-08	U-234	1.4E-13	1.4E-09	(c)
Neptunium	0.001	4,250.	7.3E-08	Np-237	5.2E-11	1.0E-06	(c)
Plutonium	0.001	38,394.	7.3E-08	Pu-238	2.1E-09	4.2E-05	(c)
				Pu-239	3.0E-09	2.0E-07	(c)
				Pu-240	4.9E-09	2.1E-07	(c)
				Pu-241	1.8E-11	2.9E-06	(c)
				Pu-242	1.6E-11	1.9E-07	(c)
Americium	0.0001	4,304.	7.3E-09	Am-241	2.3E-08	5.2E-07	(c)
				Am-243	1.4E-10	1.8E-07	(c)
Curium	0.001	4.4	7.3E-08	Cm-244	1.1E-09	540,000.	1.3E-05

(a) Various other solubility data exist, some with higher and some with lower values for various nuclides. These other data may be no more or no less applicable for this preliminary analyses.

(b) The radium, thorium, and neptunium grow larger with time, so that at 10,000 years these inventories are 6.7E-01, 49.5, and 8,243 grams per package, respectively.

(c) This value is not computed unless the primary (10^{-5}) standard is not met indicated by a value greater than one in the preceding column.

Table 7.3 Comparison of nuclide inventories presented in Tables 6-27 and 6-36 of the Richton Dome EA.

Element	300 year Package Inventory(1) (gms)	Isotope	200 year Package Inventory(2) (gms)
Carbon	831	C-14	1.25
Selenium	279	Se-79	26.8
Strontium	750	Sr-90	16.3
Technetium	3813	Tc-99	3525
Tin	6752	Sn-126	12,435
Iodine	1157	I-129	120
Cesium	7077	Cs-135	1758
		Cs-137	43
Radium	0.0011	Ra-226	5.6×10^{-4}
Thorium	1.2	Th-230	0.7
Uranium	4.8×10^{6}	U-234	1369
		U-238	4.4×10^{6}
Neptunium	4250	Np-237	3473
Plutonium	38394	Pu-238	123
		Pu-239	23424
		Pu-240	10551
		Pu-241	0.29
		Pu-242	2005
Americium	4304	Am-241	4304
		Am-243	405
Curium	4.4	Cm-244	0.03
		Cm-245	4.02

(1) From Table 6-36 of the Richton Dome EA.
(2) Adapted from Table 6-27 of the Richton Dome EA.

released to saturate the incoming brine then, assuming the isotopic fraction of C-14 is the ratio of C-14 from Table 7.1 to the carbon inventory of Table 6-36 of the Richton Dome EA, there is only 4.3×10^{-5} gm C-14/yr released. This is 3.8×10^{-5} of the 1000 year inventory as presented in Table 7.2. A more conservative approach would have been to assume that all of the carbon released was radioactive C-14. In this case, 0.029 gm C-14 would be released which is 2.5×10^{-2} of the 1000 year inventory.

In conclusion, there is an inconsistency in the mass inventory of the nuclides presented in Tables 6-27 and 6-36 of the Richton Dome EA. Furthermore, based on the information provided in the EA it is not possible to reproduce the solubility limited activity releases presented in Table 6-36 of this EA. Until the method of calculating these nuclide inventories is explained and justified, the conclusions drawn as to the waste package meeting the controlled release criteria are subject to question. This problem is common to all seven salt sites as tables similar to 6-27 and 6-36 in the Richton Dome EA appear in the other salts EA's.

APPENDIX A - REVIEWS OF DOE AND RELATED WASTE PACKAGE DATA

LIST OF REPORTS/PAPERS REVIEWED IN APPENDIX A

Allen, C.C., D.L. Lane, R.A. Palmer and R.G. Johnston, "Experimental Studies of Packing Material Stability," In the *Scientific Basis for Nuclear Waste Management, VII*, G.L. McVay, Editor, North Holland, New York, P. 105.

Anantatmula, R.P., C.H. Delegard, and R.L. Fish, "Corrosion Behavior of Low Carbon Steels in Grande Ronde Basalt Groundwater in the Presence of Basalt/Bentonite Packing," in *Scientific Basis for Nuclear Waste Management VII*, Vol. 26, G.L. McVay, Editor, Elsevier, New York, 1984, pp. 113-120.

Carter, J.P. and S.D. Cramer, "Field Stress Corrosion Tests in Brine Environments of the Salton Sea Known Geothermal Resource Area," Paper No. 203, Corrosion/80, National Association of Corrosion Engineers, 1980.

Coles, D.G. and M.J. Apted, "The Behavior of ^{99}Tc in Doped Glass/Basalt Hydrothermal Tests," in *Scientific Basis for Nuclear Waste Management VII*, Vol. 26, G.L. McVay, Editor, Elsevier, New York, 1984, pp. 129-136.

Davis, R.B. and Z.A. Munir, "Corrosion Resistance of Various Metals and Alloys in Synthetic Geothermal Brines," J. Materials Sci. *12*, 1909 (1977).

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WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Measurements of the physical, chemical and mineralogical changes in backfill material for use in a nuclear waste repository in basalt. Determination of the long time effects of temperature and pressure on the stability of the engineered barrier system.

MATERIAL

Wyoming bentonite approximately 85% sodium montmorillonite plus minor montronite, silica, feldspar, illite, calcite and gypsum. Basalt from the Umtanum flow of the Columbia River Basalt Group. Synthetic groundwater prepared to simulate reference repository groundwater.

TEST CONDITIONS

Bentonite dehydration experiments and hydrothermal tests on bentonite and water and bentonite + basalt + water using Dickson-type rocking autoclaves and cold seals.

Bentonite dehydration : 250°-550°C ; atmospheric pressure

Hydrothermal tests		mass ratio water/solids	days
Bentonite + water (autoclave)	200°C	10	60
Bentonite + water (autoclave)	300°C	10	217
Bentonite + water (cold seal)	300°C	1	341
Bentonite + basalt + water (autoclave)	150°C	10	120
Bentonite + basalt + water (autoclave)	300°C	10	89
Bentonite + basalt + water (cold seal)	300°C	1	179

METHODS OF ANALYSIS

1. Thermo-gravimetric analyses, x-ray diffraction and differential scanning calorimetry were used to identify the thermal effects on bentonite.

2. Analysis of hydrothermal reaction products using x-ray diffraction, scanning electron microscopy and energy dispersive spectrometry.

3. Solution chemistry after hydrothermal tests was determined by using ion chromatography and inductively-coupled plasma-atomic emmission spectrometry.

AMOUNT OF DATA

(a) Four data points are given which bracket the effect of long term heating of bentonite. These data focus on the structural changes of bentonite that affect its swelling capabilities.

(b) It is stated that silicon, sodium chloride and sulphate are increased by up to a factor of seven from original groundwater concentrations.

Other hydrothermal tests point to initial increases in aluminum, potassium, calcium and sodium. A single graph indicating concentration vs. time of silicon, potassium and aluminum is given.

(c) Reaction products of halite, quartz, albite and plagioclase feldspar are identified.

(d) Micrographs are presented which identify four minerals and grain etching of basalt.

UNCERTAINTIES IN THE DATA

Individual data points are given only for the concentration changes of the basalt/bentonite/water system as a function of time. Smooth curves intersect most of the points indicating consistent analytical procedures.

DEFICIENCIES IN THE DATA BASE

Canister material was not included in the tests. This could alter the solution chemistry and the reaction products in addition to the reaction rate.

APPLICATION OF DATA TO LICENSING

[Key Data ( ), Supporting Data (X)]

GENERAL CONCLUSIONS

The bentonite dehydration tests demonstrate that structural changes do not occur in bentonite after being heated continuously at 370°C for 340 days. Bentonite's ability to swell and rehydrate does not appear to diminish.

The paper points out that reactions do occur in the range of 150° to 300°C between bentonite, basalt and groundwater. Because of the duration of these experiments, approximately one year, it is believed that the rate of reaction will not be detrimental to repository performance. This is evidenced by observation of steady state reaction rates within the one year period.

The results of these tests, because of their duration, are significant. They should serve as a basis for additional research that include all of the repository components.

ORGANIZATION

Rockwell Hanford Operations.

AUTHORS/REFERENCE

Allen, C. C., Lane, D. L., Palmer, R. A. and Johnston, R. G., "Experimental Studies of Packing Material Stability," In the Scientific Basis for Nuclear Waste Management, VII, G. L. McVay, Editor, New York, North Holland, p. 105.

AVAILABILITY

Published in a Proceedings volume.

KEY WORDS

Backfill, engineered barrier, bentonite, basalt, groundwater.

DATE REVIEWED

May 1985.

ABSTRACT

The Basalt Waste Isolation Project is conducting experiments to assess the stability of bentonite (sodium montmorillonite) and crushed basalt as waste package packing materials in a nuclear waste repository in basalt. The experiments are designed to identify changes in physical, chemical, and minerological properties that these materials could undergo in the repository environment. A series of bentonite dehydration experiments showed that after 1 year at 370°C the clay's structural and swelling properties were preserved and only reversible dehydration occurred. At 440°C, however, irreversible dehydration, collapse of the clay structure, and loss of swelling ability took place. Hydrothermal tests using bentonite, or an equal mixture of bentonite and basalt, along with synthetic groundwater, were also conducted. A bentonite + water experiment showed negligible structural alteration at 200°C, although some iron enrichment of the clay occurred. At 300°C, partial conversion of the montmorillonite to an iron- and potassium-rich smectite occurred, along with the formation of secondary quartz and albite. An experiment in the basalt + bentonite + water system at 150°C resulted in partial etching of the basalt grains, but no detectable change in rock or clay mineralogy. At 300°C, the basalt was strongly etched. Furthermore, iron- and potassium-rich smectite apparently replaced montmorillonite as the dominant clay, and secondary silica, zeolites, and minor feldspar were formed. These mineral assemblages are thought to be metastable at 300°C, based on natural analogs. The kinetics and reaction paths of further transformations of packing materials are important areas for continued study.

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Low-carbon steel uniform corrosion rate data at 150°C and 250°C in basaltic water (with and without basalt/bentonite packing present).

MATERIALS

AISI 1006, 1020, and 1025 low carbon steel sheet. Test specimens measured 12.7 x 12.7 x 1.5 mm. The 75 wt % basalc/25 wt % bentonite packing was made up from -115 to +250 mesh Umtanum basalt and Baroid Wyoming bentonite. Synthetic Grande Ronde groundwater was prepared and adjusted to pH 9.75 by adding NaOH.

TEST CONDITIONS

All tests were conducted in a teflon-lined autoclave.

Oxic Tests: Specimens immersed in 10 mL of air-equilibrated Grande Ronde basaltic water. Tests run for 1 or 2 weeks at 150°C.

Anoxic Tests: Samples embedded in basalt/bentonite packing saturated with argon-sparged groundwater (dissolved oxygen level $\leq$ 0.1 mg/L). Autoclave assembled in an argon glove box to minimize air ingress to the system. Tests run for 1 or 2 weeks at 150 and 250°C.

METHODS OF ANALYSIS

All specimens after testing were cleaned of corrosion products using 1.7 M HCl, inhibited by 0.26 wt % formaldehyde. Weight losses were measured per ASTM Standards. Specimens and corrosion products were characterized by X-ray diffraction, optical metallography, and scanning electron microscopy.

AMOUNT OF DATA

For the oxic tests, each of the three steels was tested for 1 and 2 week durations. There were usually triplicate tests for each individual test condition, giving a total of 17 data points for the corrosion rate.

A similar test matrix was employed for the anoxic tests and there are 19 data points for the 150°C tests and 18 for the 250°C tests.

Optical and scanning electron micrographs are given describing the internal and surface structure of both as-received and corroded specimens.

UNCERTAINTIES IN THE DATA

The weight loss data for the triplicate samples usually show very consistent behavior. The range of values is often much less than about ± 30 percent from the average value.

DEFICIENCIES IN THE DATA BASE

The data obtained, while showing the benefits of packing material on corrosion rates, are of limited usefulness since gamma irradiation effects were not considered. There is little difference in the weight loss values for the 1 or 2 week tests and the 150°C and 250°C tests, showing that corrosion effectively stops when all of the available oxygen is used up. If gamma irradiation were present, then radiolytic oxygen would be available to continue the corrosion process. Thus, the results obtained in this study are not likely to be conservative.

No weld metal data are given.

APPLICATION OF DATA TO LICENSING

[Key Data ( ), Supporting Data (X)].

GENERAL COMMENTS

The test procedures used are excellent, and this is reflected in the low levels of scatter in the triplicated tests. For licensing, however, longer-term tests will be needed with gamma irradiation fields included.

ORGANIZATION PRODUCING DATA

Rockwell Hanford Operations.

AUTHORS/REFERENCE

Anantatmula, R. P., C. H. Delegard, and R. L. Fish, "Corrosion Behavior of Low Carbon Steels in Grande Ronde Basalt Groundwater in the Presence of Basalt/Bentonite Packing," in Scientific Basis for Nuclear Waste Management VII, Vol. 26, G. L. McVay (Editor), Elsevier, New York, 1984, pp. 113-120.

AVAILABILITY

Published as conference proceedings.

KEY WORDS

Low-carbon steel, uniform corrosion, basalt, bentonite, packing material, metallography.

DATE REVIEWED

May 1985.

ABSTRACT

Three low-carbon steels (AISI 1006, AISI 1020, and AISI 1025) were tested at 150° and 250°C in Hanford Grande Ronde Basalt groundwater (9.75 pH) under anoxic conditions (< 0.1 mg/L oxygen in water) in packing (75 wt% basalt + 25 wt% bentonite) for 1 and 2 weeks. Testing was initially performed in air-equilibrated groundwater (oxic conditions) without packing at 150°C. The average corrosion under anoxic conditions with packing was at least a factor of seven lower than that for oxic conditions at 150°C. The data indicated that carbon composition apparently affects the corrosion of low-carbon steel under oxic conditions. Under anoxic conditions with packing, corrosion was independent of the carbon composition of the steel as evidenced by almost equal weight losses for all three steels at 150° and 250°C. The weight loss at 250°C was about the same as that at 150°C due to the formation of a very adherent layer of iron-rich clay on the surface of the steel at 250°C, reducing the rate at which corrosion proceeds. Pitting was not detected in any of the specimens. Assuming linear corrosion kinetics, extrapolation of the 2-week data to 1,000 yr resulted in approximately 12 mm penetration of the low-carbon steel in Grande Ronde Basalt groundwater under anoxic conditions with packing.

5/22/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

U-bend stress corrosion data for seven iron and nickel base alloys in Salton Sea geothermal brine under hydrothermal conditions.

MATERIAL

1020 carbon steel, Type 430 stainless steel, E-Brite 26-1, Type 316L stainless steel, Hastelloy G, Hastelloy C-276 and Inconel 625. Salton Sea brine from Magmamax well.

TEST CONDITIONS

Specimen:	Rectangular U-bend 2.5 cm x 10.2 cm. Degreased and cleaned before testing.
Environment:	a) Wellhead brine at 178, 207 and 229°C. b) Steam prepared fom brine at 178 and 207°C.
Duration:	30 days.

METHOD OF ANALYSIS

After the test, the specimens were examined visually under a low power microscope and a scanning electron microscope to observe any cracks. Metallographic examination of some specimens was also conducted in cross-section and after etching.

AMOUNT OF DATA

a) Stress corrosion data in terms of cracks detected, or cracks not detected.

b) Photomicrographs showing transgranular stress corrosion cracking (SCC) and branch cracking in Type 316L stainless steel.

c) Photomicrographs showing both transgranular and intergranular SCC in Type 430 stainless steel as well as the E-Brite 26-1 alloy.

d) The pH (at 25°C) and chloride concentration in the test brine, and the liquid obtained after condensing the steam phase.

UNCERTAINTIES IN THE DATA

The susceptibility of each alloy to SCC has been stated qualitatively depending on whether any cracks were observed; no quantitative description of crack length or rate of crack growth has been measured. However, five or six specimens of each alloy were tested to observe SCC. The mean values of test conditions have been listed in a table, but the variation of actual conditions from mean values is not mentioned.

DEFICIENCIES IN THE DATA BASE

A major deficiency in the information presented in this paper arises due to the fact that the test conditions are substantially different from those expected in a repository. For example, the composition of Salton Sea brine (not given) is expected to be different from those expected in a repository. Also, the test duration of 30 days is too short on the repository time scale and no radiation was included in the tests. Quantitative information on crack growth due to stress corrosion will be needed in modeling the life of a HLW canister.

APPLICATION OF DATA TO LICENSING

[Key Data ( ), Supporting Data (X)]

GENERAL COMMENTS

The informaiton that SCC occurs in Type 430 and 316L stainless steels and E-Brite 26-1 alloy is useful in screening the alloys for use in a salt repository. It is particularly noteworthy that cracks developed even in the steam phase where chloride ion concentration was an order of magnitude lower than in the liquid phase. However, relative corrosivity of steam and brine is not reported.

It is reported that 1020 carbon steel, Hastelloy G, Hastelloy C-276 and Inconel 625 did not show SCC. This observation does not mean that these alloys are immune to SCC, and cracking cannot be ruled out when test duration is increased. However, it may be concluded that austenitic steels and the E-brite alloy are more prone to SCC in a brine environment than the other four alloys.

ORGANIZATION PRODUCING DATA

Avondale Research Center, Bureau of Mines.

AUTHORS/REFERENCE

Carter, J. P. and S. D. Cramer, "Field Stress Corrosion Tests in Brine Environments of the Salton Sea Known Geothermal Resource Area," Paper No. 203, Corrosion/80, NACE, 1980.

AVAILABILITY

Published in a Proceedings volume.

KEY WORDS

Stress corrosion cracking, Salton Sea brine, U-bend, iron base alloys, nickel base alloys.

DATE REVIEWED

June 1985.

ABSTRACT

Not given. Summary and conclusions are given below:

SUMMARY AND CONCLUSIONS

Evaluation of the stress-corrosion characteristics of seven iron- and nickel-base alloys in Salton Sea KGRA process environments has shown:

(1) Type 316 L stainless steel undergoes transgranular stress-corrosion cracking in both brine and steam environments. It is highly susceptible to SCC and, in view of other work, does not appear to be a suitable material of construction for use in the Salton Sea KGRA.

(2) Since Type 316L stainless steel is more resistant to corrosion in these geothermal process environments than most other austenitic steels, it is doubtful that many austenitic stainless steels can be used successfully as construction materials.

(3) Type 430 stainless steel undergoes both transgranular and intergranular SCC. The utility of this alloy in Salton Sea KGRA brines will depend on its Kiscc stress level in these brines and the ability during plant construction and operations to keep metal stresses below this Kiscc level.

(4) E-Brite 26-1 undergoes both transgranular and intergranular SCC in the steam environments and in the brine from the first-stage separator. The utility of this alloy, like that of Type 430 SS, will depend on its Kiscc in

the brine and the ability to keep metal stresses below this value. Also, this alloy should be tested for longer periods, perhaps 60 to 120 days, to determine if it is really resistant to SCC in the brine from the second-stage flasher.

(5) Although Hastelloys C-276 and G and Inconel 625 showed no evidence of SCC, tests of longer duration should be conducted since previous work has indicated that these metals are susceptible to SCC. Also, there is sulfide present in these brines, and nickel alloys are highly susceptible to stress-corrosion cracking in sulfide environments.

(6) 1020 carbon steel showed no evidence of stress corrosion in these environments.

6/25/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Measurements of the concentrations of Tc-99 released from 76-68 borosilicate glass in 200°C basaltic groundwater in the presence and also the absence of crushed basalt.

MATERIAL

(a) Starting waste form consisted of 7 mm dia. Tc-99 doped glass beads (PNL 76-68). These had previously been leached at 22°C. They were reused in these solubility experiments because they were to be crushed, and this would give fresh unleached surfaces. A -40 to +100 mesh fraction was ultrasonically cleaned for 2 min. to remove fine particles and mixed with an equal weight of undoped 76-68 glass which was similarly prepared. The final calculated activity of the glass was 12.5 μCi Tc-99/g glass and the concentration was 0.7 μg Tc-99/g glass.

(b) Umtanum basalt used in some tests.

TEST CONDITIONS

Uses Dickson-type autoclaves with reactants enclosed in an inert gold reaction bag.

(a) For glass tests, 19.4 g of glass was mixed with 193.6 mL of synthetic BWIP groundwater to give an initial solution to solid ratio of 10:1.

(b) For glass + basalt tests, about 10 g of glass was mixed with about 10 g of crushed basalt of -120 to +230 mesh size. The fluid volume was 200.8 mL, again giving a solution to mass ratio of 10:1.

All tests were run at 200°C at 30 MPa pressure, for up to approximately 2600 hours. Solution samples taken periodically for analysis.

METHODS OF ANALYSIS

Solution samples were taken and split, and variously diluted, filtered, acidified and submitted for radiochemical, inductively coupled plasma emission spectroscopy (ICP), and ion chromatographic (IC) analyses. The three radiochemical samples obtained after splitting a fluid sample were (1) an unfiltered sample, (2) a 4000Å (0.4 μm pore) filtered sample, and (3) an 18Å filtered sample. It was assumed that material passing through the 4000Å filter was either colloidal or in solution and the material passing through the 18Å filter was in solution.

Solid specimens were analyzed after completion of each test. Analytical techniques included optical microscopy, X-ray powder diffraction, analytical scanning electron microscopy (SEM), and analytical scanning/transmission electron microscopy (STEM).

AMOUNT OF DATA

(a) For unfiltered solutions there are 10 data points giving Tc-99 concentrations (mg/L) for glass-only reactions, and 9 data points for glass + basalt reactions.

(b) For solutions filtered through the 4000Å filter, there are 10 data points giving Tc-99 concentrations for glass-only reactions, and 10 data points for glass + basalt interactions.

(c) For the solutions filtered through the 18Å filter, there are 10 data points giving Tc-99 concentrations for glass-only reactions, and 6 data points for glass + basalt reactions. The latter concentration measurements were terminated when the Tc-99 levels fell below the detection limits (0.005 mg/L) for the instrumentation used.

UNCERTAINTIES IN THE DATA

Error bars are shown usually for the long-term tests where the Tc-99 concentrations in solution are low (2×10^{-2} mg/L). The error bars represent counting errors. For the shorter term tests, the Tc-99 levels are much higher and errors in the estimated Tc-99 concentrations are very low. Data points are always on a smooth curve drawn through the results, again showing consistent analytical procedures.

DEFICIENCIES IN THE DATA BASE

The results obtained in this work are of value since they show how the Tc-99 levels in 200°C solution are affected by the presence of basalt. However, the following deficiencies in the data base are noticeable:

(a) Umtanum basalt is not considered to be a likely host rock for the BWIP repository; thus the data are only useful as a qualitative guide.

(b) The 76-68 glass was doped with Tc-99 only, rather than a complete range of long lived radionuclides.

(c) There should be lower temperature runs to simulate actual conditions after the 300-1000 year containment period. Test temperatures such as 75, 100 and 150°C should be used to allow extrapolation of solubility results.

(d) Additional tests should include bentonite clay to allow Tc-99 concentrations to be estimated for the packing material region.

(e) The decrease in Tc-99 concentration in the glass + basalt tests was attributed to the attainment of reducing groundwater conditions because of basalt/water interaction. Measurements of dissolved oxygen level as a function of time could have given support to this speculation.

APPLICATION OF DATA TO LICENSING

[Key data ( ), Supporting data (X)].

GENERAL COMMENTS

The authors state that glass remaining from prior leach testing was used because of availability. Non-prototypic basalt was also used in the work. However, the results are of value in demonstrating that, with respect to Tc-99 solubility, the presence of basaltic material is beneficial, leading to very low concentrations of this radionuclide in solution.

The test procedures appear to be well designed and should be capable of generating valuable solubility data for appropriate waste package tests in the future.

ORGANIZATION PRODUCING DATA

Pacific Northwest Laboratory and Rockwell Hanford Operations.

AUTHORS/REFERENCE

Coles, D. G. and M. J. Apted, "The Behavior of ^{99}TC in Doped Glass/Basalt Hydrothermal Tests," in Scientific Basis for Nuclear Waste Management VII, Vol. 26, G. L. McVay (Editor), Elsevier, New York, 1984, pp. 129-136.

AVAILABILITY

Published as conference proceedings.

KEY WORDS

76-68 glass, basalt, hydrothermal tests, Tc-99, solubility, colloids.

DATE REVIEWED

May 1985.

ABSTRACT

The release of polyvalent radionuclides from a nuclear waste repository located in basalt may be sensitively related to the redox potential (Eh) imposed by the basalt. A series of tests are reported here, evaluating the effect of basalt on the concentration of ^{99}Tc released into solution from a borosilicate glass waste form. Crushed PNL76-68 glass, doped with 0.7 mg ^{99}Tc/g glass, was reacted with reference basalt groundwater under oxic hydrothermal conditions in a sampling autoclave, both alone and in the presence of crushed basalt. The steady state fluid concentrations of ^{99}Tc and various stable species were determined from samples obtained at the test conditions of 200°C, 30 MPa, and a initial solution to solid mass ratio of 10 for both tests.

In the glass + groundwater test, the ^{99}Tc concentration rose rapidly to about 50 mg/L after only 200 hr of run time and remained at a value between 50 and 60 mg/L throughout the duration of the test. For the basalt + glass + groundwater test, the ^{99}Tc concentration rose to an initial value of about 2.5 mg/L. At about 700 hr, the ^{99}Tc concentration began to drop rapidly until a value near the analytical detection limit (approximately 0.005 mg/L) was reached after a test duration of 1,400 hr. It is concluded that the presence of basalt in these hydrothermal experiments reduces the concentration of ^{99}Tc in solution by nearly four orders of magnitude, probably by control of solution Eh and subsequent precipitation of a solid containing a reduced form of technetium. Reaction mechanisms are discussed that can account for these observations.

5/22/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Uniform corrosion rates of eight metals/alloys including AISI 1010 steel in a synthetic geothermal brine.

MATERIAL

(a) AISI 1010 steel, stainless steel 304 and 316, Monel 400, nickel, molybdenum, titanium and niobium.

(b) Simulated Salton Sea brine with pH adjusted to ≈3 by adding hydrochloric acid. The composition of this brine is not given in the paper, but referenced elsewhere. Therefore, for the purpose of this review it is taken from the reference (Amer. J. Sci. 225, 129 (1968)) and given below. The simulated brine contained only sodium, potassium, calcium and chloride ions.

TABLE 1

Composition (in ppm by weight) of the reservoir fluid produced from the Shell No. 2 Imperial Irrigation District (IID) and Shell No. 1 State of California wells.[a]

Constituent	No. 2 IID	No. 1 State (no inner tubing string)[b]
Sodium	53,000	47,800
Potassium	16,500	14,000
Lithium	210	180
Barium	250	190
Calcium	28,800	21,200
Strontium	440	
Magnesium	10	27
Boron	390	290
Silica	400	
Iron	2,000	1,200
Manganese	1,370	950
Lead	80	80
Zinc	500	500
Copper	3	2
Silver	<1	<1
Rubidium	70	65
Cesium	20	17
Chloride	155,000	127,000
ΣCO_2	500	5,000
ΣS	30	30
Total Dissolved Solids	259,000	219,500

[a] The compositions reported here are for the formation fluid at the depth of production. The numbers are based on material balance calculations involving averages of a large number of brine, noncondensible, and steam condensate analyses together with measured steam qualities (wt percent steam) and ratios of noncondensibles to steam condensate. The analytical work was done by Shell Development Company, Houston, Texas, and the Colorado School of Mines Research Foundation, Golden, Colorado. With the exception of silver and copper, constituents present in trace concentrations have been omitted from the table.

[b] The No. 1 State well was produced with and without an internal 3½-inch tubing string inside the 7⅝-inch casing in the hole. The tubing string, which was 4500 feet long, acted as a downhole choke and changed (reversibly) the performance characteristics of the well. Presumably, different fractures contribute the bulk of the fluid produced by the well, depending on whether the well is equipped with an inner tubing string. These fractures are located at depths of 4575 and 4750 feet.

TEST CONDITION

Temperature: 296, 333 and 368 K.
Maximum test duration: 12 h to 8 days. Maximum test time for the 1010 sheet was 18 h.
Environment: Simulated Salton Sea brine. The initial pH was adjusted to ≈3 but it varied between 2.5 and 4 during the test. Oxygen concentration in brine varied between 8 and 10 ppm.

METHODS OF ANALYSIS

Uniform corrosion rates were determined from weight loss measurements on the coupons which were cleaned after the test using ASTM Standard Method G1-72.

AMOUNT OF DATA

(a) Uniform corrosion rates for AISI 1010 steel, 304 and 316 stainless steels, Monel 400 and nickel at 368, 333 and 296 K. Uniform corrosion rates for Mo, Nb and Ti only at 368 K. These rates were determined for three durations which were different for different metals.

(b) Macroscopic appearance of corrosion product on the surface of coupons after testing at 368 K for the maximum duration.

UNCERTAINTIES IN THE DATA

An estimate of the uncertainty in data is available from the scatter in corrosion rates obtained on triplicate specimens. Some of the irreproducibility in results may be due to the variation of pH, oxygen concentration or temperature; the uncertainty in these variables is not mentioned.

DEFICIENCIES IN THE DATA BASE

The uniform corrosion data presented in the paper are based on very short duration tests. Since the data are obtained only for three test durations, extrapolation to longer times will have poor reliability. It is not clear whether the simulated Salton Sea brine is as corrosive as those expected in a salt repository, especially when it does not contain corrosive magnesium ions. The maximum test temperature (95°C) is much lower than the highest repository temperature at which corrosion rates can be much higher. The data do not give any information on radiation corrosion or any forms of localized corrosion.

APPLICATION OF DATA TO LICENSING

[Key Data( ), Supporting Data (x)].

GENERAL COMMENTS

The purpose of corrosion tests reported in the paper is to evaluate relative susceptibilities of eight metals and alloys for short term use in geothermal environment containing brine, rather than long term use in a repository. Therefore, the test conditions are different from those expected in a salt repository and the data cannot be used directly. However, it may be inferred from the data that AISI 1010 shows highest uniform corrosion rates among the eight alloys. Unlike the other seven alloys, its corrosion rate appears to be increasing with time. Note that the corrosion resistance of this material perhaps has the closest resemblance to that of the reference low carbon steel.

ORGANIZATION PRODUCING DATA

University of California, Davis.

AUTHORS/REFERENCE

Davis, R. B. and Z. A. Munir, "Corrosion Resistance of Various Metals and Alloys in Synthetic Geothermal Brines," J. Materials Sci. 12, 1909 (1977).

AVAILABILITY

Published.

KEY WORDS

Uniform corrosion, geothermal brine, steel, pure metals.

DATE REVIEWED

March 1985.

ABSTRACT

The corrosion susceptibilities of various pure metals and alloys were investigated in synthetic geothermal fluids. Rates of corrosion AISI 1010 steel, Types 304 and 316 stainless steels, Monel 400 and nickel were determined at three temperatures (296, 333, and 368K); and those of the molybdenum, niobium, and titanium were determined at 368K only. Type 304 stainless steel appears to undergo an active - passive transition at a temperature range between 333 and 368K. In the passive state type 304 steel has essentially the same corrosion rate as type 316. At 368K the corrosion rate of pure nickel was approximately 2.5 times that of Monel, which in turn was twice that of type 316 stainless steel. The corrosion rates of Mo, Nb and Ti were less than one mdd at the highest experimental temperature.

as, 3/27/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Change in pressure of the gases generated due to gamma and alpha radiolysis of brine as a function of radiation dose.

MATERIAL

Synthetic Permian Basin brine modified with Cl^-, Br^-, SO_4^{-2}, and Mg^{+2}, and also a "real" brine prepared by dissolving Permian Basin salt in water.

TEST CONDITION

Gamma dose rate: 5 Mrad/h; 0.3 Mrad/h in one case.
Plenum/liquid volume: about 4.
Irradiation temperature: 75, 92 and 150°C.
Alpha dose rate: ≈2 Mrad/h from Pu-238 in brine solution.
Starting pH of brine: 0.5 - 10.0.
Total dose: 20 - 30 Grad.

METHODS OF ANALYSIS

The pressure of radiolytically produced gases was continuously monitored with a transducer. Gas compositions at the end of radiolysis were determined using a quadrupole mass spectrometer.

AMOUNT OF DATA

a) G values of H_2, H, e_{aq}, H_2O_2, OH, HO_2 and H^+, for gamma and alpha radiolysis, quoted from literature.

b) Pressure vs gamma dose plots for brine, brine with solid salt and brine with iron coupons at 75°C.

c) Pressure vs gamma dose plots for brine at 75°C containing Cl^-, Br^- and SO_4^{-2} separately as well as together.

d) Pressure vs gamma dose plot for brine with Mg^{+2}.

e) Pressure vs gamma dose plot for brines with initial pH = 2.0, 6.3 and 10.0.

f) Pressure vs alpha dose plot for brine at 75°C with initial pH = 0.5.

g) Change in pH of five solutions due to gamma radiolysis.

h) Value of Eh after alpha radiolysis.

UNCERTAINTIES IN THE DATA

All the results in the paper are given in figures which show continuous pressure vs dose plots, and no errors or uncertainty in the data are mentioned. Apparently, only one experiment was conducted for a given experimental condition and, therefore, reproducibility of the results is unknown.

DEFICIENCIES IN DATA BASE

Most of the experiments discussed in the paper were conducted at 75 or 92°C, except in one case where the gamma radiolysis was conducted at 75 as well as 150°C. The equilibrium pressure at 150°C is apparently one half of the value at 75°C, thus indicating the importance of temperature. Further experiments are needed to study radiolysis under the complete range of repository temperatures. Cl^-, Br^- and SO_4^{-2} ions are shown to be the dominant scavengers, which affect the radiolytic yield in the Permian Basin brine. However, some other brines currently in use at various laboratories contain significant amounts of BO_3^{-3} and other ions which should also be included in similar experiments.

APPLICATION OF DATA TO LICENSING

[Key Data (X), Supporting Data ( )]

GENERAL COMMENTS

The paper illustrates an important observation that the production of gases due to radiolysis of brine approaches a plateau at high pressures. Therefore, an experiment to study the effects of these gases, particularly hydrogen, on the performance of waste package should include such pressures (i.e. 100 atmospheres or higher). We note that the experiments in this paper emphasize the gaseous products of radiolysis whereas in a repository the species produced in liquid phase will also be important.

The H_2/O_2 ratio in the present experiments is reported as approximately equal to the stoichiometric value. However, the value of Eh equal to 1.2 volt at the end of the alpha irradiation suggests that the oxidizing and reducing species are not balanced; the cause of oxidizing conditions in the solution remains to be determined.

ORGANIZATION

Pacific Northwest Laboratory.

AUTHORS/REFERENCE

Gray, W. J., and S. A. Simonson, "Gamma and Alpha Radiolysis of Salt Brines," Presented at the 1984 Annual Meeting, Materials Research Society, Boston.

AVAILABILITY

Published in the Proceedings of the Meeting.

KEY WORDS

Gamma radiolysis, alpha radiolysis, Permian Basin brine, equilibrium pressure.

DATE REVIEWED

June 1985.

ABSTRACT

Gamma radiolysis of Permian Basin brine leads to equilibrium gas pressure of about 100 atm. at 75°C and about 40 atm. at 150°C, providing the gas space is very small and/or the total dose is very high. Dose rate dependence is being investigated but is not yet established. Alpha radiolysis of Permian Basin brine is still being evaluated, but it is clear that equilibrium gas pressures will be much higher than with gamma radiolysis. In addition, alpha radiolysis of brine results in a very high solution redox potential. Gas compositions in all cases have been about two parts H_2 to one part O_2. Efforts to simulate these results with computer models have been quite successful.

rt
6/18/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Uniform, crevice, pitting, welding and stress corrosion of 23 metals and alloys in a high temperature, high pressure, hypersaline geothermal brine containing controlled amounts of oxygen, methane and carbon dioxide.

MATERIAL

Iron based: Sandvik 3Re-60, E-Brite 26-1, 316L SS, Carpenter 20 SS, 1020 carbon steel, 4130 steel, Cor-Ten B, Mariner, 430 SS
Nickel based: Monel 400, Inconel X-750, Inconel 625, Hastelloy S, Hastelloy G, Hastelloy C-276
Copper based: 70-30 cupronickel
Titanium based: titanium, Ti-1.7W, Ti-2Ni, Ti-10V, Ti-0.2 Pd, TiCode-12
Molybdenum based: TZM
Test solution: Synthetic Salton Sea KGRA-type brine

TEST CONDITIONS

(a) General:
  Temperature: 232 ± 2°C
  pH: between 1 and 6
  Test Duration: 15 days
  Gases dissolved in brine: deaerated, 100 ppm O_2, 100 ppm CH_4, 250 ppm CO_2
  Specimen surface: 120-grit finish, pumiced, cleaned in water and methanol.

(b) Crevice corrosion: A 0.002 inch wide crevice was formed between two specimen surfaces held together by two thin Teflon bands.

(c) Stress corrosion: U-bend specimens tested for 15 and 30 days.

(d) Weld corrosion: Specimens were butt-welded according to ASTM procedure.

METHODS OF ANALYSIS

(a) Uniform and weld corrosion: Weight loss measurement after chemically removing adherent corrosion products. Depending on the alloy, three different cleaning solutions were used.

(b) Crevice Corrosion: weight loss measurements/actual crevice area.

(c) Pitting Corrosion: measured with optical micrometer.

(d) Stress Corrosion: microscopic examination for cracks.

AMOUNT OF DATA

(a) Composition of brine.

(b) Uniform corrosion rates of: all metals and alloys in deaerated brine; all iron based alloys except Sandvik 3-Re-60 and Carpenter 20 SS, Monel 400, Inconel 625, Hastelloy C-276, 70-30 cupronickel, Ti, Ti-2Ni, Ti-0.2 Pd and TiCode-12 in brine containing 100 ppm O_2 or CH_4; E-Brite 26-1, 316L SS, Cor-Ten B, Mariner, Monel 400, Inconel 625, cupronickel, Ti and Ti-0.2 Pd in brine containing 250 ppm CO_2. For eleven materials data are compared with earlier field tests.

(c) Semiquantitative crevice corrosion data for: all materials except TiCode-12 in deaerated brine; E-Brite 26-1, 316L SS, Inconel 625, Hastelloy C-276, cupronickel, 1020 carbon steel, and all titanium alloys except Ti-1.7W and Ti-10V in 100 ppm O_2 brine; E-Brite 26-1, 316L SS, 4130 steel, 430 SS, Monel 400, Inconel 625, Hastelloy C-276, cupronickel, Ti, Ti-0.2 Pd and TiCode-12 in 100 ppm CH_4 brine. Seven materials were also tested in 250 ppm CO_2 brine but no crevice corrosion was noticed. For E-Brite 26-1, 316L SS and Hastelloy S the data are compared with previous field results.

(d) Stress corrosion cracking reported as detected or not detected for all alloys except Mariner and Cor-Ten B in deaerated brine; selected eleven alloys were also tested in the other three brines. 1020 carbon steel was not tested in O_2 and CO_2 containing brines.

(e) Pitting corrosion data for all alloys in deaerated brine; fourteen materials were also tested in the other three brines. 1020 carbon steel was not tested in CO_2 containing brine. For 1020 carbon steel, 4131 steel, 430 SS, E-Brite and 316L SS data are compared with previous field tests.

(f) Effect of welding on uniform corrosion rate of 1020 carbon steel, 4130 steel, 316L SS, E-Brite 26-1, Ti, Ti-0.2 Pd and Inconel 625 in deaerated and 100 ppm oxygen containing brine.

(g) Average uniform corrosion rates of 1020 carbon steel and Cor-Ten B steel as a function of pH.

(h) SEM micrographs of 316L SS, Ti, Inconel 625, Hastelloy C-276 and E-Brite 26-1 stress corroded specimens.

UNCERTAINTIES IN DATA

It is stated that duplicate samples were used in tests of 15 and 30 days duration. However, the data for various kinds of corrosion as presented in tables and a figure show that only one test was conducted for a particular test condition. Therefore, information on the localized modes of corrosion, which is sensitive to statistics, may be of limited value i.e. an alloy might be susceptible to pitting or crevice corrosion even when it is not observed in a single test. The concentration of dissolved gases has been calculated from its partial pressure in the gas phase, not from direct measurements. Metallurgical conditions (microstructure, heat treatment and composition) of test specimens are not described. The temperature of test solution in autoclave was maintained within ±2°C.

DEFICIENCIES IN THE DATA BASE

The tests were conducted in synthetic Salton Sea KGRA-type brine which may not be as corrosive as the most corrosive brine expected in a repository, especially when it contains very little of the corrosion enhancing magnesium ions. Most of the tests were conducted only for the duration of two weeks. Therefore, the data cannot be used to predict an alloy performance on the repository time scale. Since localized corrosion modes usually have an incubation time before corrosion can be detected, the two week test period may be too short to initiate and detect these forms of corrosion. Stress corrosion performance has been described only as 'detected' or 'not detected,' which is not sufficient for quantitative design. Similar qualitative description of pitting is given for several cases. The effect of pH is investigated only on uniform corrosion rates, but it is also important in other forms of corrosion. For these data to be applicable to a salt repository, further tests incorporating radiation should be conducted.

APPLICATION OF DATA TO LICENSING

[Key Data( ), Supporting Data (X)].

GENERAL COMMENTS

The objective of this investigation was to identify a material from 23 alloys which is most suitable for use in geothermal environment comprising of brines at high temperatures. Since repository conditions can be significantly different from the geothermal environment, the data may not be of direct use. Nevertheless, these results can be used to assess the relative susceptibility of various alloys to corrosion in brine at high temperatures. A comparison of laboratory and in situ test data demonstrates that the assumption of deaerated conditions underground may not be correct. The susceptility of the alloys to various forms of corrosion are shown to be very different. Therefore, to select the best alloy a weight factor would be needed for different kinds of corrosion and the material cost.

ORGANIZATION PRODUCING DATA

Bureau of Mines, Avondale, MD.

AUTHORS/REFERENCE

Needham, P. B., S. D. Cramer, J. P. Carter and F. X. McCawley, "Corrosion Studies in High-Temperature, Hypersaline Geothermal Brines," Paper No. 59, Corrosion /79, National Association of Corrosion Engineers, 1979.

AVAILABILTIY

National Association of Corrosion Engineers

KEY WORDS

Uniform corrosion; pitting; crevice corrosion; stress corrosion; cracking; weld corrosion; geothermal brine; iron, nickel, titanium and molybdenum based alloys.

DATA REVIEWED

March 1985

ABSTRACT

Abstract not provided. Summary and conclusions attached.

SUMMARY AND CONCLUSIONS

General corrosion rates for the metals and alloys in the deaerated brine were below 127 μm/y. The reduction of brine pH below the range of 3 to 4 sharply increased the corrosion rate of low-alloy steels above an acceptable level. Based on combined analyses of the crevice corrosion, pitting corrosion, and stress-corrosion cracking results, E-Brite 26-1, Hastelloy C-276, Ti-1.7W, Ti-2Ni, Ti-10V, TZM, Ti-0.2Pd, and Ti Code-12 were the most corrosion-resistant metals and alloys in the deaerated brine. Although the general-corrosion rate of 4130 steel was moderately high, it is now a low-cost alloy and has other desirable physical and mechanical properties that make it useful for geothermal plant construction with a limited service life design. In the case of low-alloy steels, unannealed welds accelerated the corrosion of the alloys. This could be a serious problem since, in the field, there is no provision for annealing the welds.

The introduction of O_2 into the brine as a result of brine processing will appreciably change the observed corrosion characteristics of both welded and nonwelded metals and alloys. Inconel 625, Hastelloy C-276, and E-Brite 26-1 had poor corrosion resistance in oxygenated brine. On the other hand, Ti-2Ni (and possibly the other titanium alloys) had excellent corrosion resistance in the oxygenated brine, probably because of the more favorable conditions for forming a passive film on the surface. The addition of CH_4 to the brine reduced the effects of general corrosion, crevice corrosion, SCC, and pitting corrosion on most of the metals and alloys. In the case of the nickel alloys, CH_4 increased their susceptibility to crevice corrosion. The addition of CO_2 increased the susceptibility of the ferrous alloys to general corrosion and pitting but had no effect on the corrosion rates of the other metals. Although the amounts (100 to 250 ppm) of the gases used in these tests may have been somewhat higher than those that will actually be found in the Salton Sea KGRA geothermal brines, the results indicate the extent of the effects which these gases can have on the corrosion rates of the materials tested.

Most importantly, localized corrosion effects varied considerably with alloy composition and dissolved gas content. Examples include pitting in Type 316 L austentic stainless steel and in Type 430 and E-Brite 26-1 ferritic stainless steels; crevice corrosion in low allow steels and in titanium; and stress-corrosion cracking in Hastelloy C-276 and Inconel 625 when the brines contained dissolved oxygen.

Comparison of the laboratory results with the results obtained in field tests has shown that measurements in fully deaerated brines tend to underestimate the corrosion rates obtained for low-alloy steels in an operational geothermal brine environment. Similarly, except for 1020 carbon steel, the deaerated brine results underestimate the pitting-corrosion rates observed in comparable field tests.

as, 3/24/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Measurements of the corrosion rates (mils/y) of low-carbon steel, cast iron, 2-1/2 Cr-1 Mo steel and titanium-based alloys in basaltic water in the presence and absence of high gamma irradiation fields.

MATERIALS

The following metals and alloys were studied:

(a) Cast ductile iron (ASTM A536-77, Grade 60-40-80)
(b) 2-1/2 Cr-1 Mo cast steel
(c) 1025 cast steel (ASTM A536-77, Grade 60-30)
(d) 1020 wrought steel
(e) Titanium Grade 2 (commercially pure Ti)
(f) Titanium Grade 12 (Ti - 0.8%; Ni - 0.3% Mo)

Umtanum basalt was used to precondition the test solutions.

TEST CONDITIONS

Tests all carried out in autoclaves in which synthetically prepared Grande Ronde basaltic water was passed through at about 35 mL/h. The water was obtained from a reservoir sparged with an Ar/20% O_2 mixture to give 6-8 mg/L of dissolved oxygen in the incoming solution. The solution entered at the base of the autoclave, passing through a bed of crushed basalt to condition it before it reached the metal specimens.

Irradiation-corrosion tests were run at 250°C at gamma dose rates up to 2×10^6 R/h. The general corrosion tests were carried out at 150 and 250°C.

METHODS OF ANALYSIS

After exposure, iron-based materials were examined for weight loss by stripping oxide films by abrasion and immersion in formaldehyde-inhibited HCl. In the case of Ti alloys, the analcime and anhydrite layers were stripped and the weight gain measurement used to calculate the rate of metal loss.

X-ray diffraction techniques are used to identify corrosion products.

AMOUNT OF DATA

There are 11 data points for the irradiation-corrosion rate as a function of time for the ductile iron; 12 for 2-1/2 Cr-1 Mo steel; 2 for 1025 cast steel, and 5 for 1020 wrought steel. The data were plotted on a graph and compared with a corrosion rate band for unirradiatd tests. For the titanium-based materials, uniform corrosion rates are given from weight gain measurements made after 10-month irradiation-corrosion tests at 250°C. Additional data were obtained on hydrogen pickup for the titanium-based alloys during the exposures. It was found that after a 10-month test the hydrogen pickup was largest for specimens exposed to the higher gamma dose rates. At a dose rate of 10^6 R/h, Grade-12 titanium showed an increase in hydrogen level of up to 160 ppm, and Grade-2 titanium had an increase of up to about 105 ppm. There are 10 data points each for Grades 12 and 2 titanium for the hydrogen pickup levels.

UNCERTAINTIES IN THE DATA

As expected, for these types of tests there is considerable scatter in the uniform corrosion rate and hydrogen pickup data. For the iron-based materials, several duplicate tests commonly show a factor of 2 difference in the rates of corrosion at 250°C. Nevertheless, it is possible to estimate a maximum credible corrosion rate as a function of time. Based on the results over exposure times to 13 months, the long term corrosion rate appears to be less than about 0.5 mil/y.

In the case of hydrogen pickup levels, there is only a small amount of scatter in the values for Grade-12 titanium when plotted as a function of gamma dose rate. On the other hand, for Grade-2 material, there is a significant amount of scatter in the hydrogen levels. The largest and smallest values for a given dose rate may differ by a factor of about 2.

DEFICIENCIES IN THE DATA BASE

The results from this paper are valuable as detailed screening studies to determine the more appropriate container materials. Currently, low-carbon steel is the reference container material for BWIP. Unfortunately, the amount of data given in the paper for this steel is very limited and short-term compared to the other metals that were tested.

Bentonite/crushed basalt packing should be included in the tests to simulate interactions between the container and packing. It may have a beneficial effect by limiting water migration to the metal and the altered rates of corrosion should be evaluated. Long term tests (up to 5 years) would be desirable in order to check if new failure mechanisms such as hydrogen embrittlement and stress-assisted failure could occur. Lower, more prototypic, gamma dose rate data are also needed.

APPLICATION OF DATA TO LICENSING

[Key data ( ), Supporting data (X)].

GENERAL COMMENTS

The data are of value and could be used to give conservative estimates of the uniform corrosion rates of a container in a basalt repository, provided the actual container temperature is no greater than the maximum test temperature used (250°C). However, other failure modes could appear for very long test times, and such testing is needed. Pitting, in fact, was observed for the cast iron and it could also occur in the other iron-based materials after extended exposures.

Data on weld metal must be generated.

ORGANIZATION PRODUCING DATA

Pacific Northwest Laboratory

AUTHORS/REFERENCE

Nelson, J. L., R. E. Westerman, and F. S. Gerber, "Irradiation-Corrosion Evaluation of Metals for Nuclear Waste Package Applications in Grande Ronde Basalt Groundwater," in Scientific Basis for Nuclear Waste Management VII, Vol. 26, G. L. McVay (Editor), Elsevier, New York, 1984, pp. 121-128.

AVAILABILITY

Published as conference proceedings.

KEY WORDS

Carbon steels, cast iron, 2-1/2 Cr-1 Mo steel, Grade-2 titanium, Grade-12 titanium, irradiation-corrosion, uniform corrosion, hydrogen pickup, pitting, BWIP, basalt, container, gamma irradiation.

DATE REVIEWED

May 1985.

ABSTRACT

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

dt, 5/22/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Chemical changes induced in natural rock salt and synthetic NaCl by heat and gamma irradiation.

MATERIAL

Palo Duro rock salt from the G. Friemal Core Hole No. 1; Paradox basin rock salt from Gibson Dome GD1 Core Hole; and Synthetic single crystal NaCl.

TEST CONDITION

Gamma Irradiation: Source - ^{60}Co
Dose rate - 5×10^{5} to 5×10^{6} R/h
Temperature - 50 to 150°C

Heat Treatment: Temperature - 50 to 500°C for both irradiated and unirradiated samples.
Heating rate - 50°C/h

METHODS OF ANALYSIS

Chemical changes in salt were determined from the analysis (pH, titration, UV-visible spectroscopy) of the solution obtained by dissolving the specimens in water. Thermal desorption - mass spectrometry and Gran titration were used to measure the composition of gases generated due to heating.

AMOUNT OF DATA

Radiation damage (as hypochlorite ion concentration in solution) at 50 and 150°C for NaCl and Palo Duro Basin rock salt as a function of radiation dose. Time dependence of hypoclorite ion concentration in solution at 50, 70 and 90°C. Changes in the pH and total base content of Palo Duro Basin rock salt solutions as a result of heating at 190°C for 30 h, and irradiating to $5 \times 10^{[illegible]}$ R.

Concentration of HCl, H_2S, SO_2, and CO_2 generated as a function of temperature when Paradox Basin salt was heated. Results of Gran titration for salt samples heated to 90, 150, 190 and 300°C for up to 30 hours.

UNCERTAINTIES IN THE DATA

From the error bars shown on the figures for hypochlorite ion concentra-tion an uncertainty in the data is estimated to be up to approximately 44%. For total base in solution this estimate is ≈23%; the tabulated data give the range of uncertainty between ± 5% and ± 10.3%. Reproducibility of the thermal desorption/mass spectrometry analysis is not given. The uncertainty in pH values is given as ± 0.3 units.

DEFICIENCIES IN DATA BASE

The results described in this paper are based on a very small number of experiments. Although rock salt specimens were obtained from two locations in Palo Duro and Paradox Basin deposits, respectively, it would be premature to draw a general conclusion regarding the heat and gamma irradiation properties of salt at a repository horizon. The thermal desorption/mass spectrometry results have identified the generation of HCl, H_2S, SO_2, and CO_2 but a quantitative analysis of each gas remains to to be determined. It will be useful to determine the response of salt to heating and irradiation when brine is also present.

APPLICATION OF DATA TO LICENSING

[Key Data (X), Supporting Data ( )]

GENERAL COMMENTS

An important conclusion described in this paper is that the chemical changes induced in rock salt by heat can be more important than radiation damage. In particular, the evolution of acidic gases could initiate or enhance various forms of container corrosion. However, an extensive testing program would be needed to determine the range of concentration of these corrosive gases corresponding to the salt specimens from different locations. A related testing program should then focus on the detrimental effects of these gases on different waste package components.

The author has suggested that radiation damage to salt will not alter the near-field chemical environment unless chlorine gas escapes from the damaged salt because hypochlorite to chlorate disproportionation occurs rapidly. In this regard, we may note that under continuous irradiation in a repository hypochlorite concentration will not continue to decay to zero but will reach an equilibrium value.

ORGANIZATION PRODUCING DATA

Pacific Northwest Laboratory

AUTHORS/REFERENCE

Pederson, L. R., "Chemical Implications of Heat and Radiation Damage to Rock Salt", Presented at the 1984 Annual Meeting, Materials Research Society, Boston.

AVAILABILITY

To be published in the Proceedings of the meeting.

KEY WORDS

Rock salt, heat effects, gamma radiation effects, acidic gases.

DATE REVIEWED

June 1985.

ABSTRACT

Chemical changes induced in Palo Duro and Paradox Basin natural rock salts and in synthetic NaCl by heat and gamma radiation were investigated. Heating of unirradiated natural rock salts to 300°C resulted in HCl (most prevalent), SO_2, CO_2, and H_2S evolution, and increased the base content of the remaining salt by not more than 10 microequivalents per gram; whereas, heating of synthetic NaCl gave no product. Gamma irradiation produced sodium colloids and neutral chlorine in amounts similar to the results of Levy and coworkers. When the irradiated salts were heated, three reactions were apparent: (1) radiation-induced defects recombined; (2) neutral chlorine was evolved; and (3) HCl, SO_2, and H_2S were evolved, similar to results for unirradiated salts. Because reaction (1) appeared to dominate over reaction (2), it is expected that the influence of radiation damage to salt on the near-field chemical environment will be minor.

rt, 6/18/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Susceptibility to uniform corrosion of three candidate canister alloys in salt at high temperatures.

MATERIAL

(a) Cor-Ten A (a low alloy steel containing 1% Cr, 0.5% Ni and 0.35% Cu); ASTM A516 low carbon steel; 304L stainless steel.

(b) Salt from Carlsbad, New Mexico.

TEST CONDITIONS

Temperature: 80, 225 and 600°C
Duration: 1000, 5000 or 10,000 hours.
Environment: sealed or unsealed capsules containing salt pieces.

METHOD OF ANALYSIS

(a) The thickness of the corrosion film was measured directly using a micrometer, or with the help of optical and scanning electron microscopes.

(b) Corrosion products were analyzed using x-ray diffraction, scanning electron microscope and x-ray energy spectrometry techniques.

AMOUNT OF DATA

(a) Appearance of Cor-Ten A, A516 and 304L alloys after 10,000 h tests.
(b) Uniform corrosion value of 304L stainless steel and A-516 steel after 1000 and 5000 h at 80, 225 and 600°C under sealed tube conditions.
(c) Composition of glass waste form and brine, which will be used in the proposed experiments.
(d) 9 micrographs of cross-sections of 304L stainless steel and low carbon steel specimens.

UNCERTAINTIES IN THE DATA

The thickness measurements using micrometer showed too large uncertainty to give useful data. The uncertainty with traveling stage microscope was

≈5 mil. Thickness measurements with SEM were most accurate but the uncertainty estimate is not given for this case. Except for the test of low carbon steel at 600°C, the corrosion penetration is reported as <2 mil which is presumably the detection limit in the method used. It is not clear whether replicate specimens were used under any of the test conditions.

DEFICIENCIES IN THE DATA BASE

(a) The alloy specimens were exposed to Carlsbad rock salt at atmospheric pressure. However, in a salt repository the salt/alloy interface can be at much higher lithostatic pressure. The corrosion rate under latter conditions can be much different than those given in the present paper.

(b) Significant corrosion was observed in sealed capsules at 600°C because of easy availibility of moisture and H_2S. In a repository these two components can be present at lower temperatures. Therefore, testing is needed under repository-like conditions.

(c) Radiation was not present in any of the tests, but it is known to produce radiation damage in salt as well as to enhance corrosiveness of the environment under certain conditions.

(d) There is no information given on the possibility of localized corrosion or hot salt corrosion.

(e) To obtain reliable time dependence of corrosion, data are needed for more frequent time intervals than just after 1000 and 5000 hours.

APPLICATION OF DATA TO LICENSING

[Key Data (X), Supporting Data ( )].

GENERAL COMMENTS

The paper discusses preliminary results of corrosion of three canister alloys in dry rock salt. However, dry salt conditions are not considered as corrosive as wet salt or brine conditions. The more corrosive conditions would develop due to the migration of moisture in grain boundaries, or brine cavities towards hot canister surfaces.

Therefore, the authors have proposed testing in brine solutions made from Carlsbad salt; however, note that more corrosive brine compositions containing higher concentration of magnesium ions are also possible in a repository.

AUTHORS/REFERENCE

Rankin, W. N., "Canister Compatibility with Carlsbad Salt," Paper No. 212, Corrosion/80, National Association of Corrosion Engineers, 1980.

AVAILABILITY

Published in a Proceedings volume.

KEY WORDS

Uniform corrosion, Carlsbad salt, 304L stainless steel, A516 low carbon steel.

DATE REVIEWED

March 1985

ABSTRACT

No significant reaction was found when candidate canister alloys were heated with salt from Carlsbad, New Mexico, for up to 5000 hours in sealed capsules and for up to 10,000 hours in unsealed capsules at temperatures (80 and 225°C) that bracket the maximum temperature calculated for reference SRP waste containers at 20-foot spacings in salt. Additional tests were made at 600°C in sealed capsules to characterize reactions that may occur between candidate canister alloys and any component of the salt that is released when decrepitation occurs. Under these extreme conditions there was no significant attack of Type 304L stainless steel. But there was up to 20-mils attack of the low-carbon steel. Additional long-term heating tests in sealed capsules are being planned to characterize the attack of these alloys by both the volatile components of the salt and by Carlsbad salt brine at the temperature expected during final storage of waste forms.

as, 4/1/85

WASTE PACKAGE DATA REVIEW FORM

TYPE OF DATA

Uniform corrosion rates of two mild steels and one cast iron in moist salt environment.

MATERIAL

(a) ASTM A216 Grade WCA mild steel - as cast, homogenized (930°C for 24 h, air cool), and normalized (930°C for 1 h, air cool). This alloy is the reference overpack material.

(b) AISI 1025 wrought steel sheet.

(c) ASTM A536 Grade 60-40-18 ductile cast iron.

(d) Reagent grade NaCl and its brine solution in deionized water.

(e) Simulated Permian Basin brine and salt (PBB1 and PBB3).

TEST CONDITIONS

Temperature: 150°C.
Duration: 1 and 3 months under static conditions.
Environment: Moist salt with 0 to 30 wt % water and 0 to 3 wt % magnesium. Anoxic atmosphere containing Ar and He.

METHODS OF ANALYSIS

Uniform corrosion rates were determined from weight loss measurements. Corrosion product was examined using X-ray diffraction and some unspecified chemical techniques.

AMOUNT OF DATA

(a) Composition of PBB1 and PBB3 brines.

(b) Uniform corrosion rates of A216 cast steel, A536 cast iron and 1025 wrought steel in PBB1 salt moistened with varying amounts of PBB3 brine.

(c) Uniform corrosion rates of as cast, normalized and homogenized A216 steel in dried NaCl with NaCl brine, dried PBB1 salt with PBB1 brine, and dried PBB1 salt with PBB3 brine.

(d) A figure showing dependence of corrosion rates of A216 steel on magnesium concentration.

UNCERTAINTIES IN THE DATA

The stated corrosion rates are average of four test specimens for each test condition. From the figures in the paper, we find uncertainties in corrosion rates ranging from 5% to 48%; the highest uncertainty is for the A216 cast steel under high moisture conditions. However, the variation of test parameters such as temperature or magnesium concentration is not stated.

DEFICIENCIES IN THE DATA BASE

(a) The data are reported only for very limited test conditions which are not necessarily the worst possible in a salt repository. For example, magnesium which is shown to be the most important corrosion causing ion had a maximum concentration of 3 wt%, whereas inclusion brines in a repository can have higher values.

(b) An important repository parameter, radiation, has not been evaluated.

(c) The specimens are not examined for any localized corrosion.

(d) The tests were run for only two test durations from which it is difficult to obtain reliable predictions on repository time scale.

APPLICATION OF DATA TO LICENSING

[Key Data ( ), Supporting Data (X)].

GENERAL COMMENTS

This paper contains important results which demonstrate the corrosiveness of magnesium ions in a moist salt environment. However, the results are very preliminary and little is known about the mechanism of corrosion or other factors which might enhance the rate of corrosion. The present tests were conducted under anoxic condition, but brine radiolysis in repository can produce oxidizing conditions as well. The role of changing pH such as due to colloidal sodium or localized corrosion will need to be determined.

ORGANIZATION PRODUCING DATA

Pacific Northwest Laboratory.

AUTHORS/REFERENCE

Westerman, R. E. and S. G. Pitman, "Corrosion of Candidate Iron-Base Waste Package Structural Barrier Materials in Moist Salt Environments," paper presented at Materials Research Society Meeting, Boston, MA., November 1984.

AVAILABILITY

Published as Conference proceedings. Also available as PNL-SA 12344.

KEY WORDS

Uniform corrosion, mild steel, cast iron, moist salt, magnesium ions.

DATE REVIEWED

March 1985.

ABSTRACT

Mild steels are considered to be strong candidates for waste package structural barrier (e.g., overpack) applications in salt repositories. Corrosion rates of these materials determined in autoclave tests utilizing a simulated intrusion brine based on Permian Basin core samples are low, generally <25 μm (1 mil) per year. When the steels are exposed to moist salts containing simulated inclusion brines, the corrosion rates are found to increase significantly. The magnesium in the inclusion brine component of the environment is believed to be responsible for the increased corrosion rates.

as, 3/19/85

APPENDIX B - SAMPLE CALCULATION OF NUCLIDE INVENTORY

A sample calculation for the C-14 is given below.

From Table 7.1 the total curies of C-14 in spent fuel at 200 years is given as:

M = 87,300 curies per 72,000 MTHM
= 1.21 curies/MTHM

To convert this to grams per package, multiply by the number of MTHM per package, 4.6, to obtain:

M = 5.57 curies/package

Next divide by the specific activity, which for C-14 is 4.45 curies/gm. This yields

M = 1.25 grams/package.

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13. ABSTRACT (200 words or less)

Detailed evaluations continued on DOE reports and papers concerned with the evaluation of waste package component behavior. The intent was to estimate the quantity and relevance of data being generated for barrier system performance analysis. In addition, several review studies have been completed to evaluate progress in the DOE waste package program. These include work on the selection of a glass composition for West Valley, New York, high level waste, a description of the system at West Valley for vitrifying the waste, and reviews of papers included in the Defense High-Level Waste Leaching Program and the recent Tucson, Arizona, "Waste Management '85" Conference.

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